www.mtg.in | June 2015 | Pages 92 | ₹ 30

SOLVED PAPERS 2015

AIPMT • KERALA PMT • WB JEE

CHEMISTRY today

India's #1
CHEMISTRY MONTHLY FOR
JEE (Main & Advanced) & PMTs

NCERT CORNER

Chemistry Musing

Concept Map

ACE YOUR WAY CBSE XII
SERIES 1

Advanced Chemistry Bloc

Challenging Problems

LEARN Fast

Olympiad Problems

You Ask ?

We Answer ✓

Concept Booster

mtG
Trust of more than
1 Crore Readers
Since 1982

2015-1000-00701

CHEMISTRY today

Vol. XXIV No. 6 June 2015

Corporate Office :
Plot 99, Sector 44 Institutional area,
Gurgaon -122 003 (HR). Tel : 0124-4951200
e-mail : info@mtg.in website : www.mtg.in

Regd. Office
406, Taj Apartment, Near Safdarjung Hospital,
Ring Road, New Delhi - 110029.

Managing Editor : Mahabir Singh
Editor : Anil Ahlawat (BE, MBA)

Contents

Owned, Printed and Published by Mahabir Singh from 406, Taj Apartment, New Delhi - 29 and printed by Personal Graphics and Advertisers (P) Ltd., Okhla Industrial Area, Phase-II, New Delhi. Readers are adviced to make appropriate thorough enquiries before acting upon any advertisements published in this magazine. Focus/Infocus features are marketing incentives MTG does not vouch or subscribe to the claims and representations made by advertisers. All disputes are subject to Delhi jurisdiction only.
Editor : Anil Ahlawat

editorial

Science Teaching in Schools – Below Danger Mark

Alarm bells ringing! Science is not taught in all senior secondary schools under the Delhi Government. Out of 877 senior government schools, only 270 teach science in classes XI and XII. This gives a double body blow to an education system. First, this puts the lower income groups permanently in the lower level as it is the students who study in government schools, who are below the well off line. They cannot afford to pay the high fees and special fees demanded by private schools of the top classes. The private schools on their part cannot afford to give high class education with first class facilities for science laboratories unless they charge the parents.

The government cannot say that they lack money to give first class teaching facilities in the schools run by them. This is the first priority of the government. We cannot afford to keep the lower middle classes in the lower level in the next generation also. The first priority of the government is to give emphasis to give a first class education to all. Every socialist country does it. I do not mean communist countries but countries like France and countries in North Africa. Students do not depend on their parents for education up to any level. The second body blow is to keep the have–nots away from higher scientific education. People choose art subjects in colleges because of their choice. A minimum level science education up to the college level is a must for the development of the nation.

All our dreams of industrialisation and advancement in every field should be supported by the state governments. The syllabus for every school, particularly state government schools should be same as followed by central schools with NCERT textbooks. If the schools do not have the ability to recruit good teachers, let NCERT recruit and train the teachers who alone should teach in high schools which cannot keep science subjects for lack of teachers.

Anil Ahlawat
Editor

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 23

JEE MAIN/PMTs

1. Pick up the rearrangement involving migration to electron deficient oxygen.

(a) Pinacol – pinacolone rearrangement

(b) Hofmann rearrangement

(c) Baeyer – Villiger rearrangement

(d) None of these

2. Which among the following statements is correct regarding the bonding of Pt and C_2H_4 in Zeise's salt?

I. It involves σ-donation from the π-orbital of alkene into vacant metal hybrid orbital.

II. It involves π-donation from the π-orbital of alkene into vacant metal hybrid orbital.

III. It involves π-back donation from the filled metal *d*-orbital (or hybrid) into the vacant antibonding orbital of alkene.

(a) I, II and III (b) I and III

(c) II and III (d) III only

3. The vapour pressures of benzene, toluene and xylene are 75 torr, 22 torr and 10 torr respectively at 20°C. Which of the following is not a possible value of the vapour pressure of an equimolar binary/ternary solution of these at 20°C? Assume all form ideal solutions with each other.

(a) $48\frac{1}{2}$ (b) 16

(c) $35\frac{2}{3}$ (d) $53\frac{1}{2}$

4. Ethylene can be prepared in good yield by

(a) $CH_3CH_2N^+(CH_3)_3I^- \xrightarrow{\text{Heat}} CH_2{=}CH_2 + (CH_3)_3N + HI$

(b) $CH_3CH_2N^+(CH_3)_3OH^- \xrightarrow{\text{Heat}} CH_2{=}CH_2 + (CH_3)_3N + H_2O$

(c) $CH_3CH_2NH_2 \xrightarrow{\text{Heat}} CH_2{=}CH_2 + NH_3$

(d) both (a) and (b).

5. The IP_1, IP_2, IP_3, IP_4 and IP_5 of an element are 7.1, 14.3, 34.5, 46.8, 162.2 eV respectively. The element is likely to be

(a) Na (b) Si

(c) F (d) Ca

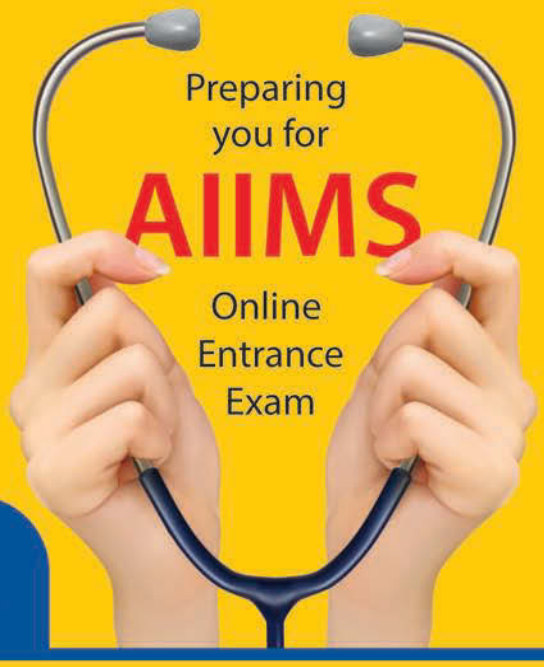
Solution Senders of Chemistry Musing

SET 22

1. Krunal N. Jariwala (Ahmedabad)
2. Pramila Kar, Cuttack (Odisha)
3. Manas Rajput, Udaipur (Rajasthan)

This year AIIMS MBBS Entrance exam is an ONLINE EXAM

mtG



To make you test-ready
MTG is launching

mtG Rank Indicator Online Test Series for AIIMS

There are five tests, exactly on the pattern of AIIMS exam. Each test comprises of

- 60 Physics Questions (40 MCQs + 20 A&R)
- 60 Biology Questions (40 MCQs + 20 A&R)
- 60 Chemistry Questions (40 MCQs + 20 A&R)
- 20 General Knowledge MCQs

This is not all, you will also get

- Question Bank of 200 General Knowledge MCQs FREE.
- Experts support in solving your queries.
- Complete performance analysis in each test.

Rewards for Meritorious Students!

- Student securing First Rank in each test will be refunded the complete Test Series Fee.
- If a test series student gets selected in AIIMS he/she will be awarded ₹ 2,500.

DON'T WAIT!

ENROL NOW!

Log on to www.mtg.in
or write to us on info@mtg.in
For more query call on 08800255334/35

₹599/-

Test Schedule

AIIMS Rank Indicator Test 1 - 7th May	AIIMS Rank Indicator Test 2 - 12th May
AIIMS Rank Indicator Test 3 - 17th May	AIIMS Rank Indicator Test 4 - 22nd May
AIIMS Rank Indicator Test 5 - 27th May	

JEE ADVANCED

6. In the reaction,

$$2SO_2 + O_2 \rightleftharpoons 2SO_3,$$

starting with 2 moles of SO_2 and 1 mole of O_2 in 1 L flask, mixture required 0.4 moles of MnO_4^- in acidic medium. Hence, K_c is

(a) 2.0 (b) 0.4
(c) 1.6 (d) 2.6

COMPREHENSION

Boiling point of a covalent compound depends on the intermolecular forces. Intermolecular forces are the forces of attraction and repulsion between the interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together *i.e.*, covalent bonds.

7. Liquification of which gaseous substance will arise as a result of momentary imbalance in electronic distribution?

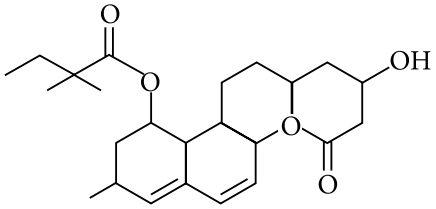
(a) $NH_{3(g)}$ (b) $CO_{(g)}$
(c) $Na^+_{(g)}Cl^-_{(g)}$ (d) $Xe_{(g)}$

8. In which of the following triads, first one has the highest boiling/melting point?

(a) PH_3, AsH_3, SbH_3
(b) HBr, HCl, HF
(c) CH_3OCH_3, CH_3SCH_3, CH_3SeCH_3
(d) AlF_3, SiF_4, PF_5

INTEGER VALUE

9. The number of stereogenic centres present in following compound is



10. 2 g of a gas *X* are introduced into an evacuated flask kept at 25°C. The pressure is found to be 1 atm. If 3 g of another gas *Y* are added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal behaviour, the molecular mass ratio of *Y* and *X* is

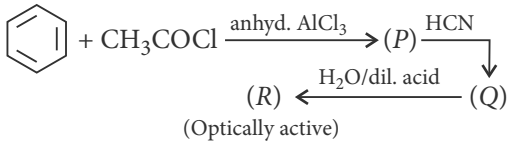
NCERT CORNER

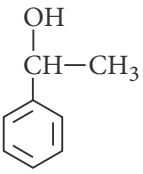
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry. Papers of JEE(Main & Advanced)/AIPMT/AIIMS/other PMTs are drawn heavily from NCERT books. Practice Hard! All the best!!

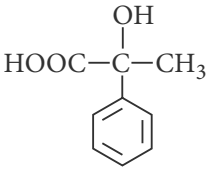
1. 0.5 mole of each of H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be

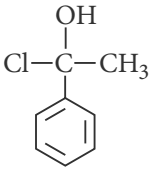
(a) $p_{SO_2} > p_{CH_4} > p_{H_2}$ (b) $p_{H_2} > p_{SO_2} > p_{CH_4}$
(c) $p_{CH_4} > p_{SO_2} > p_{H_2}$ (d) $p_{H_2} > p_{CH_4} > p_{SO_2}$

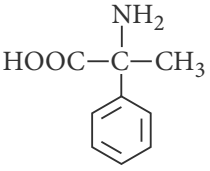
2. (*R*) in the given reaction sequence is



(a) 

(b) 

(c) 

(d) 

3. The atomic weights of two elements *A* and *B* are 40 and 80 respectively. If *x* g of *A* contains *y* atoms, how many atoms are present in 2*x* g of *B*?

(a) $\frac{y}{2}$ (b) $\frac{y}{4}$
(c) y (d) $2y$

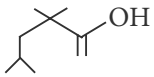
4. Phenol associates in benzene to a certain extent to form dimer. A solution containing 2.0×10^{-2} kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. The degree of association of phenol is
(K_f for benzene = 5.12 K kg mol^{-1})

(a) 73.4% (b) 50.1%
(c) 42.3% (d) 25.1%

5. Dettol is used as an antiseptic. It is a mixture of

(a) furacine, terpineol
(b) bithionol, iodoform
(c) chloroxylenol, terpineol
(d) veronal, serotonin.

6. The IUPAC name of the given compound is



(a) 2,4,4-trimethylhex-5-ene-5-ol
(b) 3,3,4,4-tetramethylbut-1-en-2-ol
(c) 3,3,5-trimethylhex-1-en-2-ol
(d) none of the above.

7. Assume two radioactive substances *A* and *B* disintegrating by

$$\frac{-d[A]}{dt} = k_A[A],\ t_{1/2(A)} = \frac{0.693}{k_A}$$

$$\frac{-d[B]}{dt} = k_B[B]^2,\ t_{1/2(B)} = \frac{1}{k_B[B]_0}$$

If both half-life periods and concentrations are equal, rates at the start of reaction will be in the ratio

(a) 0.693 (b) k_A/k_B
(c) k_B (d) none of these.

8. An example of a condensation homopolymer is

(a) bakelite
(b) melamine-formaldehyde resin
(c) alkyd resin
(d) perlon or nylon-6.

9. The Hinsberg's test of a compound, $C_5H_{14}N_2$ produces a solid that is insoluble in 10% aq. NaOH. This solid derivative dissolves in 10% aqueous sulphuric acid. Which of the following would best describe these facts?

(a) $NH_2CH_2CH_2N(CH_3)_2$
(b) $(CH_3)_2NCH_2CH_2NHCH_3$
(c) $NH_2CH_2C(CH_3)_2CH_2NH_2$
(d) $(CH_3)_2NCH_2N(CH_3)_2$

10. Correct arrangement of the following acids in decreasing order of pK_a values is

$\underset{\text{I}}{CH_3COOH}$, $\underset{\text{II}}{Cl_2CHCOOH}$, $\underset{\text{III}}{F_3CCOOH}$,
$\underset{\text{IV}}{ClCH_2COOH}$ $\underset{\text{V}}{FCH_2COOH}$

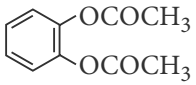
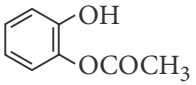
(a) I > III > II > IV > V (b) I > IV > V > II > III
(c) III > II > I > V > IV (d) II > III > I > IV > V

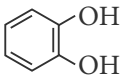
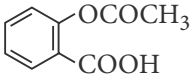
11. At 273 K, the density of a certain gaseous oxide at 2 atmosphere is same as that of dioxygen at 5 atmosphere. The molecular mass of the oxide (in g mol^{-1}) is
(a) 80 (b) 64
(c) 32 (d) 160

12. If 0.189 g of a chlorine containing organic compound gives 0.287 g of silver chloride, then the percentage of chlorine in the organic compound is
(a) 35.47 (b) 47.57
(c) 37.57 (d) 45.37

13. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE) is
(a) $[Mn(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{3+}$

14. An organic compound *P* has 76.6% C and 6.38% H. Its vapour density is 47. It gives a characteristic colour with aq. $FeCl_3$. *P* when treated with CO_2 and NaOH at 140°C under pressure gives *Q* which on acidification gives *R*. *R* reacts with acetyl chloride to give *S*, which is

(a)  (b) 

(c)  (d) 

15. Which of the following descriptions about $[FeCl_6]^{4-}$ is correct?
(a) dsp^3, inner orbital complex, diamagnetic
(b) sp^3d^2, outer orbital complex, paramagnetic
(c) d^2sp^3, inner orbital complex, paramagnetic
(d) sp^3d^2, outer orbital complex, diamagnetic

16. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
(a) $KClO_3$ (b) Na_2CO_3
(c) $NaNO_3$ (d) $CaCO_3$

17. Which of the following order about their basic strengths is correct?
(a) $NH_3 < NH_2OH < NH_2NH_2$
(b) $NH_2OH < NH_2NH_2 < NH_3$
(c) $NH_3 > NH_2OH > NH_2NH_2$
(d) $NH_2OH > NH_2NH_2 > NH_3$

18. In acidic solution, MnO_4^- is
(a) oxidised by 3 electrons
(b) reduced by 3 electrons
(c) oxidised by 5 electrons
(d) reduced by 5 electrons.

19. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are 23, 24, 25 and 26 respectively. Which one of these may be expected to have the highest second ionisation enthalpy?
(a) V (b) Cr
(c) Mn (d) Fe

20. In the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.
[Given: $\Delta G_f^\circ(N_2O_4) = 100$ kJ; $\Delta G_f^\circ(NO_2) = 50$ kJ]
The reaction will be in
(a) forward direction (b) reverse direction
(c) equilibrium (d) cannot say.

21. The data for the reaction $A + B \rightarrow C$, is

Exp.	$[A]_0$	$[B]_0$	Initial rate
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

The rate law corresponds to the above data is
(a) Rate = $k[A][B]^3$ (b) Rate = $k[A]^2[B]^2$
(c) Rate = $k[B]^3$ (d) Rate = $k[B]^4$

22. The uncertainty in the velocity of a particle of mass 6.626×10^{-31} kg is 1×10^6 m s^{-1}. What is the uncertainty in its position (in nm)? ($h = 6.626 \times 10^{-34}$ J s)
(a) $\left(\frac{1}{2\pi}\right)$ (b) $\left(\frac{2.5}{\pi}\right)$
(c) $\left(\frac{4}{\pi}\right)$ (d) $\left(\frac{1}{4\pi}\right)$

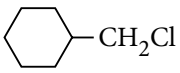
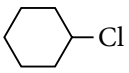
23. Which of the following orders is not in accordance with the property stated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power
(c) HI > HBr > HCl > HF : Acidic property in water
(d) F > Cl > Br > I : Electronegativity

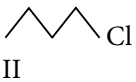
24. Calculate the amount of $Ca(OH)_2$ required to remove the hardness of water from 60,000 litres containing 16.2 g of $Ca(HCO_3)_2$ per 100 litre.
(a) 1.11 kg (b) 2.22 kg
(c) 3.33 kg (d) 4.44 kg

25. Which one of the following is least covalent in nature?
(a) NF_3 (b) BiF_3
(c) PF_3 (d) SbF_3

26 The van der Waals' constants for four gases *P*, *Q*, *R* and *S* are 4.17, 3.59, 6.71 and 3.8 atm L^2 mol^{-2}. Therefore, the ascending order of their liquefaction is
(a) $R < P < S < Q$ (b) $Q < S < R < P$
(c) $Q < S < P < R$ (d) $R < P < Q < S$

27. Which of the following haloalkanes would undergo S_N2 reaction faster?

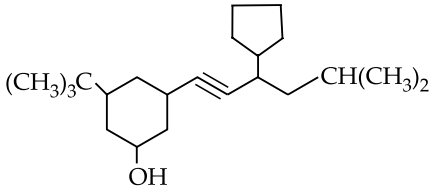
I.  II. 

III.  IV. 

(a) I (b) II
(c) III (d) IV

28. For the properties mentioned, the correct trend for the different species is in
(a) strength as Lewis acid – $BCl_3 > AlCl_3 > GaCl_3$
(b) inert pair effect – Al > Ga > In
(c) oxidising property – $Al^{3+} > In^{3+} > Tl^{3+}$
(d) first ionization enthalpy – B > Al > Tl

29. Total number of tertiary carbon atoms present in the following compound is



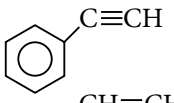
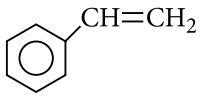
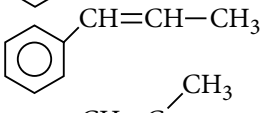
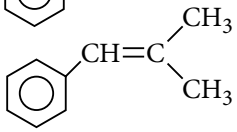
(a) 6 (b) 2
(c) 4 (d) 5

30. For a reaction, $2K_{(g)} + L_{(g)} \rightarrow 2M_{(g)}$; $\Delta U^\circ = -10.5$ kJ and $\Delta S^\circ = -44.1$ J K^{-1}. Calculate ΔG° for the reaction and predict whether the reaction will be spontaneous or non-spontaneous?
(a) + 0.16 kJ, non-spontaneous
(b) – 0.16 kJ, spontaneous
(c) + 26.12 kJ, non-spontaneous
(d) –26.12 kJ, spontaneous

31. In which of the following pairs of molecules/ions both the species are paramagnetic?
(a) C_2, N_2^+ (b) O_2^{2-}, F_2
(c) NO, CN (d) N_2^{2-}, NO^+

32. The isoelectronic pairs are
(a) Na^+, Mg^{2+} (b) Mg^{2+}, F^-
(c) NO^+, N_2 (d) all of these.

33. For $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$, $E^\circ = 1.33$ V at $[Cr_2O_7^{2-}] = 4.5$ millimole, $[Cr^{3+}] = 15$ millimole, *E* is 1.067 V. The pH of the solution is nearly equal to
(a) 2 (b) 3
(c) 5 (d) 4

34. $X \xrightarrow[\text{(Reductive)}]{\text{Ozonolysis}} Y + Z$
Y can be obtained by Etard's reaction. *Z* undergoes disproportionation reaction with concentrated alkali. *X* could be
(a)  (b) 
(c) 
(d) 

35. $P \xrightarrow[2.\ H_3O^+]{1.\ CH_3MgBr} R \xrightarrow[2.\ \Delta]{1.\ \text{dil. NaOH}}$ 4-methylpent-3-en-2-one.
P is
(a) propanone (b) ethanamine
(c) ethanenitrile (d) ethanal.

36. RbO_2 is
(a) peroxide and paramagnetic
(b) peroxide and diamagnetic
(c) superoxide and paramagnetic
(d) superoxide and diamagnetic.

37. The true statement for the acids of phosphorus, H_3PO_2, H_3PO_3 and H_3PO_4 is
(a) the order of their acidity is $H_3PO_4 > H_3PO_3 > H_3PO_2$

(b) all of them are reducing in nature
(c) all of them are tribasic acids
(d) the geometry of phosphorus is tetrahedral in all the three.

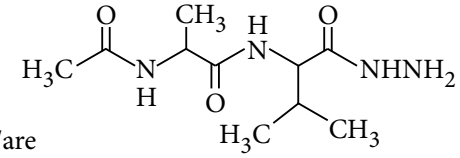
38. Initial rate data at 25°C are listed in the table for the reaction : $NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$

Exp. no.	Initial $[NH_4^+]$	Initial $[NO_2^-]$	Initial rate of consumption
1.	0.24	0.10	7.2×10^{-6}
2.	0.12	0.10	3.6×10^{-6}
3.	0.12	0.15	5.4×10^{-6}

The rate law for the reaction will be
(a) $k[NH_4^+]$ (b) $k[NH_4^+][NO_2^-]$
(c) $k[NH_4^+]^2$ (d) $k[NH_4^+][NO_2^-]^{-1}$

39. A crystalline solid *X* reacts with dil. HCl to liberate a gas *Y*. *Y* decolourises acidified $KMnO_4$. When a gas *Z* is slowly passed into an aqueous solution of *Y*, colloidal sulphur is obtained. *X* and *Z* could be, respectively
(a) Na_2S, SO_3 (b) Na_2SO_4, H_2S
(c) Na_2SO_3, H_2S (d) Na_2SO_4, SO_2

40. The number of peptide bond(s) in the compound



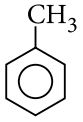
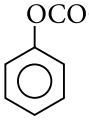
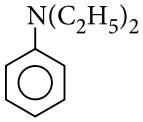
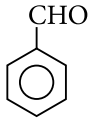
is/are
(a) 1 (b) 2
(c) 3 (d) 4

41. In a solid, oxide ions are arranged in *ccp*. One-sixth of the tetrahedral voids are occupied by cations *X* while one-third of the octahedral voids are occupied by the cations *Y*. The formula of the compound is
(a) X_2YO_3 (b) XYO_3
(c) XY_2O_3 (d) $X_2Y_2O_3$

42. In the following reactions sequence

$$CH_3CH_2Br \xrightarrow[\Delta]{aq.\ KOH} A \xrightarrow[\Delta]{KMnO_4/H^+} B \xrightarrow[\Delta]{NH_3} C \xrightarrow[alkali]{Br_2} D;$$

'*D*' is
(a) CH_3Br (b) CH_3CONH_2
(c) CH_3NH_2 (d) $CHBr_3$

43. Which of the following compounds undergo electrophilic substitution most easily?
(a) 
(b) 
(c) 
(d) 

44. The major product formed when 2-bromo-2-methylbutane is refluxed with ethanolic KOH is
(a) 2-methylbut-2-ene (b) 2-methylbutan-1-o1
(c) 3-methylbutan-2-ol (d) 2-methylbutan-2-ol.

45. Silica is reacted with Na_2CO_3. Which gas is liberated?
(a) CO (b) O_2
(c) CO_2 (d) O_3

46. Which of the following structures for a nucleotide is not correct?
(a) Cytosine-Ribose-Phosphate
(b) Uracil-2-Deoxyribose-Phosphate
(c) Uracil-Ribose-Phosphate
(d) Thymine-2-Deoxyribose-Phosphate

47. The production of dihydrogen gas via water-gas shift reaction :

$$CO_{(g)} + H_2O_{(g)} \xrightarrow[Catalyst]{\Delta} CO_{2(g)} + H_{2(g)}$$

The CO_2 gas is removed by scrubbing with solution of
(a) sodium arsenite (b) calcium oxide
(c) sodium phosphite (d) aluminium oxide.

48. In a mixture of PbS, ZnS and FeS, each component is separated from other by using the reagents in the following sequence in froth floatation process
(a) potassium ethyl xanthate, KCN
(b) potassium ethyl xanthate, KCN, NaOH, $CuSO_4$, acid
(c) KCN, $CuSO_4$, acid
(d) none of the above.

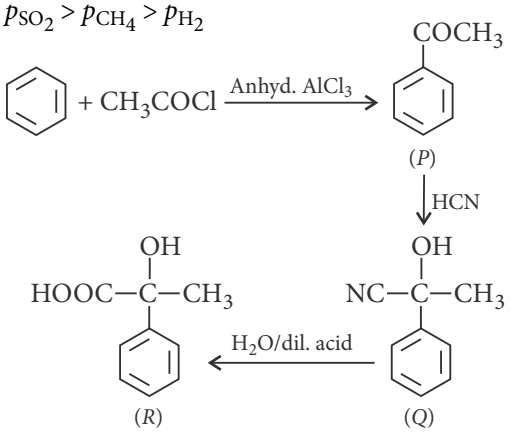
49. Biochemical Oxygen Demand (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be
(a) rich in dissolved oxygen
(b) poor in dissolved oxygen
(c) highly polluted
(d) not suitable for aquatic life.

50. The correct order of first ionisation potential among the following elements Be, B, C, N, O is
(a) B < Be < C < O < N
(b) B < Be < C < N < O
(c) Be < B < C < N < O
(d) Be < B < C < O < N

SOLUTIONS

1. **(a) :** Initially, partial pressures were equal. Now $r \propto \sqrt{1/d}$ or $\sqrt{1/M}$, therefore amounts diffused out in the same time will be $H_2 > CH_4 > SO_2$.
Amounts left will be $H_2 < CH_4 < SO_2$
$\therefore \quad p_{SO_2} > p_{CH_4} > p_{H_2}$

2. **(b) :**



(Optically active)

3. **(c) :** No. of moles of $A = \frac{x}{40}$
No. of atoms of $A = \frac{x}{40} \times N_A = y$
No. of moles of $B = \frac{2x}{80} = \frac{x}{40}$
Now, no. of atoms of $B = \frac{x}{40} N_A = y$

4. **(a) :** $M_2(\text{obs.}) = \frac{K_f \times w}{W(\text{in kg}) \times \Delta T_f}$

$$= \frac{5.12 \times 2.0 \times 10^{-2}}{1.0 \times 0.69} = 14.84 \times 10^{-2} \text{ kg mol}^{-1}$$
$$= 148.4 \text{ g mol}^{-1}$$

Calculated molecular mass of phenol = 94 g mol^{-1}

$$i = \frac{M_2(\text{cal.})}{M_2(\text{obs.})} = \frac{94}{148.4} = 0.633$$

$$\underset{1-\alpha}{2C_6H_5OH} \rightleftharpoons \underset{\alpha/2}{(C_6H_5OH)_2}$$

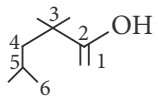
Total species $= (1-\alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$

$$i = \frac{1 - \alpha/2}{1} \text{ or } \frac{\alpha}{2} = 1 - i$$

or $\quad \alpha = 2(1-i) = 2(1-0.633) = 0.734 = 73.4\%$

5. **(c)**

6. **(c) :**



3,3,5-Trimethylhex-1-en-2-ol

7. **(a) :** $t_{1/2(A)} = t_{1/2(B)}$

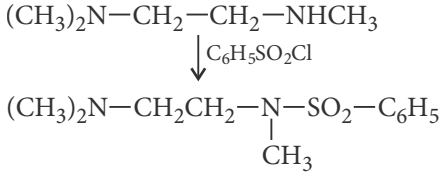
$$\frac{0.693}{k_A} = \frac{1}{k_B[B]_0}; \quad \frac{k_A}{k_B} = 0.693\ [B]_0 = 0.693\ [A]_0$$

Rate, $r_A = k_A[A]_0$; $r_B = k_B[B]_0^2 = k_B[A]_0^2$

$$\frac{r_A}{r_B} = \frac{k_A}{k_B[A]_0} = 0.693$$

8. **(d) :** Nylon-6 is a condensation homopolymer since it is obtained by condensation polymerization of only one type of monomer, *i.e.*, caprolactum.

9. **(b) :** 3° amine does not react with Hinsberg's reagent, 2° amine reacts but salt formed is not soluble in alkali.
1° amine reacts and salt formed is soluble in alkali.



Not soluble in aq. NaOH but dissolves in sulphuric acid

10. **(b) :** More the electron withdrawing effect, the compound will be more acidic. More the number of halogen atoms, greater would be the dispersion of the negative charge. Hence, more will be stabilisation of anion and the compound will be more acidic. More the value of pK_a, less acidic will be the compound. Smaller the value of pK_a, the compound will be more acidic.

11. **(a) :** From ideal gas equation, $PV = nRT$

$$PV = \frac{w}{M}RT \qquad \left(\because \quad n = \frac{w}{M}\right)$$

so, $\quad P \propto \frac{1}{M} \quad \therefore \quad \frac{P_1}{P_2} = \frac{M_2}{M_1}$

$$\Rightarrow \quad \frac{2}{5} = \frac{32}{M_1} \quad \text{or,} \quad M_1 = \frac{5 \times 32}{2} = 80 \text{ g mol}^{-1}$$

12. **(c) :** According to Carius method,
% of chlorine in organic compound

$$= \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed} \times 100}{\text{Mass of substance taken}}$$
$$= \frac{35.5 \times 0.287}{143.5 \times 0.189} \times 100 = 37.57\%$$

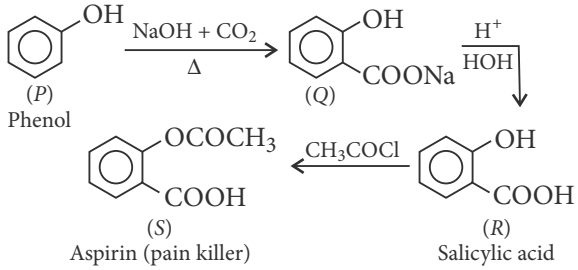
13. **(b) :** H_2O is a weak field ligand, hence $\Delta_o <$ pairing energy.
CFSE $= (-0.4x + 0.6y)\Delta_o$
where, x and y are no. of electrons occupying t_{2g} and e_g orbitals respectively.
For $[Fe(H_2O)_6]^{3+}$ complex ion,

$$Fe^{3+}(3d^5) = t_{2g}^3 e_g^2 = -0.4 \times 3 + 0.6 \times 2$$
$$= 0.0 \text{ or } 0 \text{ Dq}$$

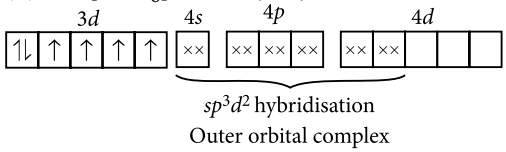
14. (d) : To determine empirical formula from data :

Element	%	Relative no. of atoms	Simple ratio
C	76.6	$\frac{76.6}{12}=6.38$	6
H	6.38	$\frac{6.38}{1}=6.38$	6
O	17.02	$\frac{17.02}{16}=1.06$	1

$\therefore$ Empirical formula (P) = C_6H_6O
Empirical formula weight = 94
Molecular weight = $2 \times VD = 2 \times 47 = 94$
$\therefore$ Molecular formula of P is C_6H_6O.
Since P gives colour with aq. $FeCl_3$ it has a phenolic group.
Compound P should be C_6H_5OH (phenol).



15. (b) : In $[FeCl_6]^{4-}$, $Fe^{2+}(3d^6)$,



sp^3d^2 hybridisation
Outer orbital complex
Paramagnetic due to presence of four unpaired electrons.

16. (d) : $CaCO_3 \xrightarrow{\Delta} \underset{\text{(Basic)}}{CaO} + \underset{\text{(Acidic)}}{CO_2}$

17. (b) : Basicity in nitrogen compounds is attributed to the availability of lone pair of electrons.
Putting more electronegative groups on N will decrease its basicity.
Therefore, the order of basicity of these compounds is :

$NH_3 > NH_2NH_2 > NH_2OH$

18. (d) : In acidic medium,
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
The reaction shows gain of $5e^-$ *i.e.* reduction.

19. (b) : The second ionisation potential value of Cr is sufficiently higher than those of neighbouring elements. This is because of the electronic configuration of Cr^+ which is $3d^5$ (half-filled), *i.e.*, for the second ionisation, the electron is to be removed from very stable configuration.

20. (b) : Standard Gibbs free energy change for the reaction, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$\Delta G^\circ = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$
$= 2 \times 50 - 100 = 0$
$\Delta G^\circ = -2.303\ RT \log K_p = 0;\ K_p = 1$
Initially, $p_{N_2O_4} = p_{NO_2} = 10$ bar

So, $Q_{p(\text{initial})} = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = 10$

Initial Gibbs free energy of the above reaction,
$\Delta G = \Delta G^\circ + 2.303\ RT \log Q_p$
$\Delta G = 0 + 2.303 \times 8.314 \times 298 \log 10$
$= 5.705 \times 10^3$ kJ mol^{-1}
Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.

21. (c) : $A + B \rightarrow C$
Let rate = $k[A]^x [B]^y$
where order of reaction is $(x + y)$
Putting the values of exp. 1, 2, and 3, we get following equations.

$0.10 = k\ [0.012]^x\ [0.035]^y$ ...(i)
$0.80 = k\ [0.024]^x\ [0.070]^y$ ...(ii)
$0.10 = k\ [0.024]^x\ [0.035]^y$ ...(iii)

Dividing eq. (ii) by eq. (iii), we get

$$\frac{0.80}{0.10} = \left(\frac{0.070}{0.035}\right)^y \Rightarrow 2^y = 8 \Rightarrow y = 3$$

Keeping $[A]$ constant, $[B]$ is doubled, rate becomes 8 times.
Dividing eq. (iii) by eq. (i), we get

$$\frac{0.10}{0.10} = \left(\frac{0.024}{0.012}\right)^x \Rightarrow 2^x = 1 \Rightarrow x = 0$$

Keeping $[B]$ constant, $[A]$ is doubled, rate remains unaffected. Hence rate is independent of $[A]$.

Rate $\propto [B]^3$

22. (d) : According to Heisenberg uncertainty principle,

$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$\Delta x = \frac{h}{4\pi \cdot m\Delta v}$ $\quad [\because \Delta p = m\Delta v]$

$= \frac{6.626 \times 10^{-34}}{4\pi \times 6.626 \times 10^{-31} \times 1 \times 10^6}$

$= \frac{1 \times 10^{-9}}{4\pi}$ m or $\frac{1}{4\pi}$ nm

23. (a) : The bond dissociation energy order is incorrect, the correct order is $Cl_2 > Br_2 > F_2 > I_2$. The lower value of bond dissociation energy of fluorine is due to the high inter-electronic repulsions between non-bonding electrons in the 2*p*-orbitals of fluorine. As a result, F—F bond is weaker in comparison to Cl—Cl and Br—Br bonds.

24. (d) : Amount of $Ca(HCO_3)_2$ in 60,000 litres of water

$$= \frac{16.2 \times 60{,}000}{100} = 9720 \text{ g} = \frac{9720}{162} = 60 \text{ moles}$$

[$\because$ mol. wt. of $Ca(HCO_3)_2 = 162$]

$$\underset{1 \text{ mole}}{Ca(OH)_2} + \underset{1 \text{mole}}{Ca(HCO_3)_2} \rightarrow 2CaCO_3\downarrow + 2H_2O$$

Amount of $Ca(OH)_2$ required = 60 moles

$= 60 \times 74 = 4440$ g $= 4.44$ kg

[$\because$ mol. wt. of $Ca(OH)_2 = 74$]

25. (b) : On moving down the group, the covalent character of halides decreases.

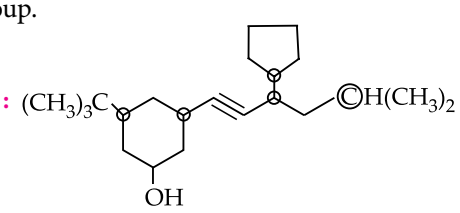
$$\underset{NF_3,\ PF_3,\ SbF_3,\ BiF_3}{\xrightarrow{\text{covalent character (decreases)}}}$$

26. (c) : Easily liquefiable gases have greater inter-molecular forces which is represented by high value of *a*. The greater the value of *a* more will be liquefiability. So, the order is $Q < S < P < R$.

27. (c) : Among I and II, I will undergo S_N2 reaction faster as it is a primary alkyl halide while II is a secondary alkyl halide. Among I, III and IV, III will undergo S_N2 reaction fastest as iodine is a better leaving group because of large size. Hence, it will be released at a faster rate in the presence of incoming nucleophile.

28. (a) : Lewis acid strength decreases down the group.

29. (d) :



Encircled carbon atoms in this compound are tertiary carbon atoms (carbon atoms directly attached to three other carbon atoms).

30. (a) : $2K_{(g)} + L_{(g)} \rightarrow 2M_{(g)}$

$\Delta n_g = 2 - 3 = -1$

$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$= -10.5 \times 10^3 + (-1 \times 8.314 \times 298)$

$= -10500 + (-2477.572) = -12977.57$ J

$= -12.98$ kJ

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -12.98 - 298\ (-44.1 \times 10^{-3})$

$= -12.98 + 13.14 = 0.16$ kJ

Since ΔG° is +ve hence, the reaction is non-spontaneous.

31. (c) : Molecular orbital configuration of

$C_2 : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2p_x^2\ \pi 2p_y^2$ (diamagnetic)

$N_2^+ : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^1$ (paramagnetic)

$O_2^{2-} : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^*2p_x^2\ \pi^*2p_y^2$ (diamagnetic)

$F_2 : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^*2p_x^2\ \pi^*2p_y^2$ (diamagnetic)

$NO : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^*2p_x^1$ (paramagnetic)

$CN : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^1$ (paramagnetic)

$N_2^{2-} : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2\ \pi^*2p_x^1\ \pi^*2p_y^1$ (paramagnetic)

$NO^+ : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2$ (diamagnetic)

32. (d) : All are isoelectronic pairs.

Na^+ and Mg^{2+} have 10 electrons.

Mg^{2+} and F^- have 10 electrons.

NO^+ and N_2 have 14 electrons.

33. (a) : For the given reaction,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$E = E^\circ - \frac{2.303RT}{nF}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

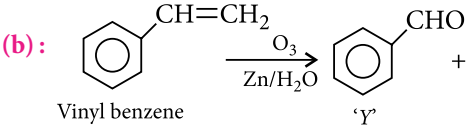
$$1.067 = 1.33 - \frac{0.0591}{6}\log\frac{[Cr^{3+}]^2[H_2O]^7}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$1.067 = 1.33 - 9.85\times10^{-3}\log\frac{[15\times10^{-3}]^2[1]^7}{[4.5\times10^{-3}][H^+]^{14}}$$

$$\frac{-0.263}{-9.85\times10^{-3}} = 2\log[15\times10^{-3}] - \log[4.5\times10^{-3}] - 14\log[H^+]$$

$$26.7 = 2\times-1.82 + 2.34 + 14\ \text{pH} \Rightarrow \text{pH} = \frac{28}{14} = 2$$

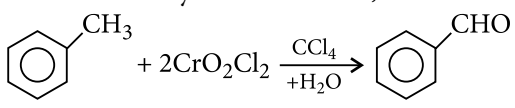
34. (b) :



Vinyl benzene (Styrene) 'X'

'Y'

'Y' is obtained by Etard's reaction,



Toluene

Benzaldehyde 'Y'

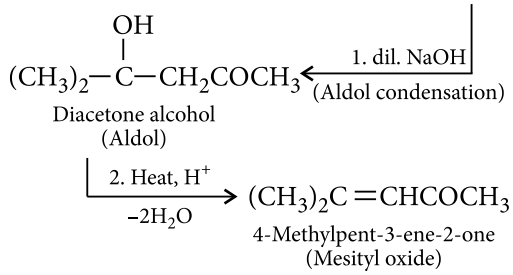
'Z' reacts with conc. NaOH,

$$\underset{\text{Formaldehyde } (Z)}{2HCHO} + NaOH \xrightarrow[\text{Cannizzaro's reaction}]{\text{Disproportionation}} \underset{\text{Sodium formate}}{HCOONa} + CH_3OH$$

35. (c) :

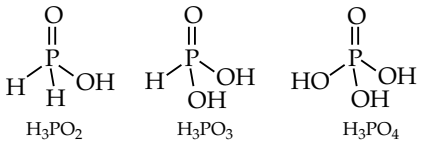
$$\underset{\text{Ethanenitrile}}{H_3C-C\equiv N} \xrightarrow[H_3O^+]{CH_3MgBr} CH_3COCH_3$$

'P' — Acetone (2 moles)



36. (c)

37. (d) : There is very little difference in their acidity.



Reducing nature depends on no. of P—H bonds. More the no. of P—H bonds, more will be the reducing nature. Thus, H_3PO_2 is stronger reducing agent than H_3PO_3 while H_3PO_4 does not act as reducing agent at all.

H_3PO_2, H_3PO_3 and H_3PO_4 contain one, two and three ionisable hydrogen atoms (P—OH bonds) respectively.

As sp^3 hybridised, therefore all are tetrahedral.

38. (b)

39. (c) : $\underset{\text{'X'}}{Na_2SO_{3(s)}} + 2HCl_{(dil.)} \rightarrow 2NaCl + \underset{\text{'Y'}}{SO_{2(g)}}\uparrow + H_2O$

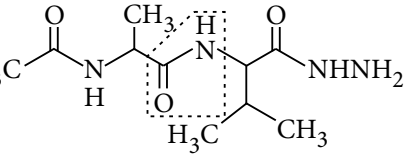
$$H_2O + SO_{2(g)} \rightarrow \underset{\text{Sulphurous acid}}{H_2SO_{3(aq)}}$$

(An aq. solution of Y)

$$\underset{\text{'Z'}}{H_2SO_3 + 2H_2S_{(g)}} \rightarrow 3S + 3H_2O$$

(Colloidal)

40. (a) :



41. (b) : Suppose number of O^{2-} ions = n. Then number of octahedral voids = n and number of tetrahedral voids = $2n$

No. of cations X present in tetrahedral voids

$$= \frac{1}{6} \times 2n = \frac{n}{3}$$

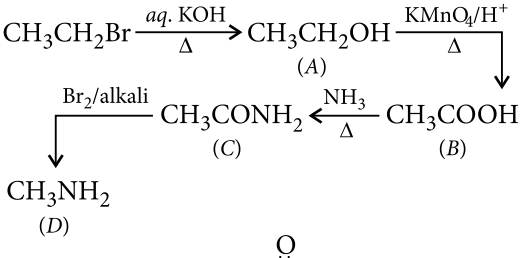
No. of cations Y present in octahedral voids

$$= \frac{1}{3} \times n = \frac{n}{3}$$

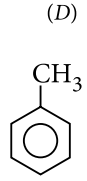
$$\therefore \quad \text{Ratio } X : Y : O^{2-} = \frac{n}{3} : \frac{n}{3} : n = 1 : 1 : 3$$

Hence, formula is XYO_3.

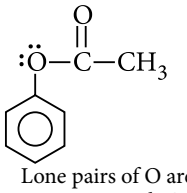
42. (c) :



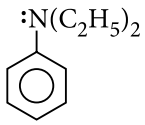
43. (c) :



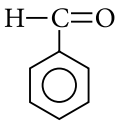
Activating due to +*I* and hyperconjugation (weak effects)



Lone pairs of O are in conjugation with C = O hence moderate activating group

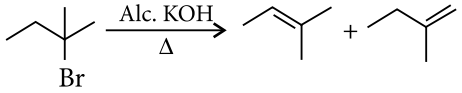


Lone pair on N leads to +*M* effect (a powerful effect) (Most activating)



Deactivating group

44. (a) : According to Saytzeff's rule, the compound undergoes elimination reaction to form more substituted alkene as the major product.



2-Bromo-2-methylbutane — 2-Methylbut-2-ene (70%) — 2-Methylbut-1-ene (30%)

45. (c) : $SiO_2 + Na_2CO_3 \xrightarrow{\Delta} Na_2SiO_3 + CO_2\uparrow$

46. (b) : Uracil is present only in RNA which contains ribose as the sugar. Thus, nucleotide given in option (b) is incorrect.

47. (a) **48. (b)**

49. (a) : Clean water rich in dissolved oxygen would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

50. (a)

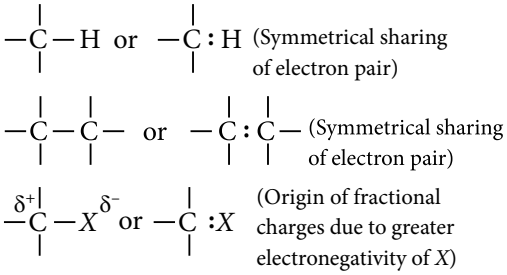
LEARN FAST

Electron Displacements in Organic Compounds

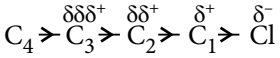
The behaviour of an organic compound is influenced to a large extent by the electron displacements taking place in its covalent bonds. These displacements may be of permanent nature or temporary which take place in presence of another species in the molecule. The acidity and basicity of organic compounds, their stability, their reactivity towards other substances, etc. can easily be predicted by considering such electronic displacements.

Inductive Effect

- This is a permanent effect operating in polar covalent bonds. The induction of a permanent dipole in a covalent bond bearing two unlike atoms of different electronegativities is referred to as the inductive effect.
- The development of partial +ve and –ve charges is due to the drift of the shared pair of electrons towards the more electronegative atom resulting in the origin of small fractional charges on the constituent atoms.
- When a carbon atom is bonded to a hydrogen (C – H) or another carbon (C – C) atom by a covalent bond such as in alkanes, the sharing of electron pair is symmetrical between them.



- The direction of displacement is shown by placing an arrow head midway along the line representing the sigma bond.



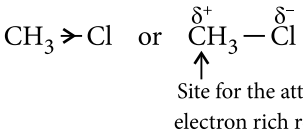
- The inductive effect of an atom or a group of atoms diminishes rapidly with distance. In fact, the inductive effect is almost negligible beyond two carbon atoms from the active atom or group.
- Inductive effect does not involve actual transfer of electrons from one atom to another but merely helps in displacing them permanently.
  - **Groups with –*I* effect :**

    $NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > C_6H_5$

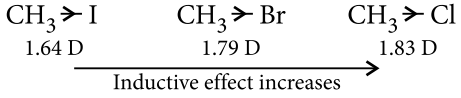
    Decreasing order of – *I* effect ⟶
  - **Groups with +*I* effect :**

    $(CH_3)_3C > (CH_3)_2CH > C_2H_5 > CH_3 > H$

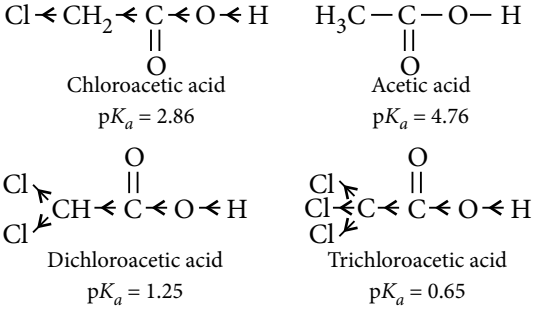
    Decreasing order of +*I* effect ⟶
- The phenomenon of inductive effect is very important in organic chemistry as it is helpful in explaining a number of facts.
  - **Reactivity of alkyl halides :** The presence of halogen atoms in the molecule of alkyl halide creates a centre of low electron density which is readily attacked by the negatively charged reagents.

  - **Dipole moment :** As the inductive effect increases, the dipole moment increases.

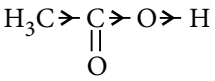
  - **Relative acid strength of chloroacetic acids and acetic acid :**

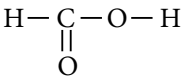
The decreasing order of acid strength :

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

- **Relative acid strength of formic acid and acetic acid :**



$pK_a = 4.76$



$pK_a = 3.77$

Methyl group has an electron releasing inductive effect (+*I* effect). Therefore acetic acid is a weaker acid than formic acid.

- **Relative acid strength of fluoroacetic acid, chloroacetic acid, bromoacetic acid and iodoacetic acid :** Halogenated acids are much stronger acids than the parent acid and the acidity increases almost proportionately with the increase in electronegativity of the halogen present which helps in repelling the proton from the hydroxy group of acid.

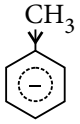
$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

  - Since the inductive effect decreases with increase in distance of halogen atom from the carboxylic group, the strength of the acid is proportionally decreased.

$CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH$
α-Chlorobutyric acid β-Chlorobutyric acid

$> CH_2(Cl)CH_2CH_2COOH > CH_3CH_2CH_2COOH$
γ-Chlorobutyric acid *n*-Butyric acid

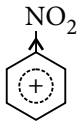
- **Relative reactivity of toluene (methylbenzene) and benzene in aromatic substitution reactions :** Aromatic substitution reactions are generally electrophilic in nature. Methyl has an electron releasing inductive effect (+*I* effect). Therefore, toluene with higher electron density is more reactive than benzene in electrophilic substitution reactions.



Toluene
(High electron density)
(More reactive towards electrophilic substitution reactions)

Benzene

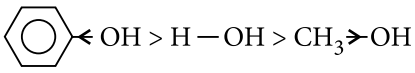
- **Relative reactivity of nitrobenzene and benzene in electrophilic aromatic substitution reactions :**



Nitrobenzene (–*I* effect due to $-NO_2$)
(Lower electron density)
(Less reactive towards electrophilic substitution reactions)

Benzene

- **Relative acid strength of water, phenol and methyl alcohol :** As compared to water, phenol is more acidic (–*I* effect) but methyl alcohol is less acidic (+*I* effect).



Phenol Water Methyl alcohol

- **Strength of base :** A compound is said to be basic in nature, if it is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing. The difference in base strength can be explained on the basis of inductive effect.
  - As compared to ammonia, methylamine is more basic (+*I* effect) while aniline is less basic and diphenylamine is a still weaker base (–*I* effect).

    $CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH$
  - The decreasing order of base strength in alcohols is due to +*I* effect of alkyl groups.

$(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$
3° 2° 1° methyl

  - Greater the tendency to donate electron pair for coordination with proton, more is the basic nature, *i.e.*, more the negative charge on nitrogen atom (due to +*I* effect of alkyl group), higher is the basic strength.

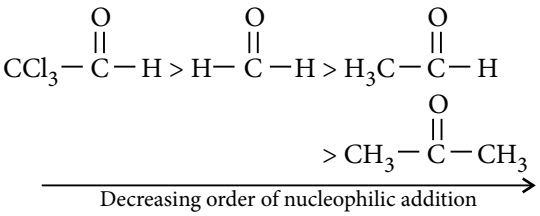
    Thus, the basic nature decreases in the order,

Alkyl group	Relative basic strength
CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5	$R_2NH > R_3N > RNH_2 > NH_3$

- **Relative stabilities of carbocations :**

$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

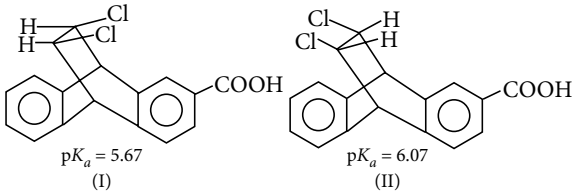
- **Reactivity of carbonyl compounds in nucleophilic addition reactions :** +*I* group increases electron availability on carbonyl carbon. This therefore decreases the rate of nucleophilic addition. On the other hand, electron withdrawing –*I* effect decreases electron availability on carbonyl carbon and thereby increases the rate of nucleophilic addition.



- Inductive effect is also dependent on the difference in the state of hybridisation of the atoms linked by covalent bond.
  - Relative acidity of hydrocarbons may be given as :
    $HC \underset{sp}{\equiv} CH > CH_2 \underset{sp^2}{=} CH_2 > CH_3 \underset{sp^3}{-} CH_3$
  - Relative basicity of corresponding carbanions is as :
    $CH_3-\bar{C}H_2 > CH_2=\bar{C}H > CH\equiv\bar{C}$
  - The acid strength of acrylic acid ($CH_2 = CHCOOH$) is considerably higher than that of propionic acid (CH_3CH_2COOH) due to the electron withdrawing inductive effect of the sp^2-hybridised carbon atom of the α,β-double bond even though the resonance effect of the α,β-unsaturated carbon system would tend to decrease the acid strength.

Field Effect

- Inductive effect is a permanent effect in the ground state of the molecule and usually operates through single bonds. However, when the inductive effect is transmitted through space or solvent molecules, it is known as field effect.
- The two chlorine atoms in (I) and (II) exert the same inductive effect with respect to the position of electrons associated with the —COOH group and consequently the two compounds should exhibit the same acid strength.

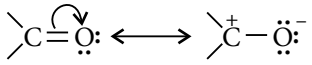


$pK_a = 5.67$ (I) $pK_a = 6.07$ (II)

However, the two chlorine atoms in the molecule (I), being closer to the acid group as compared to (II), will exert greater electron withdrawing effect in (I) as compared to (II). Hence the isomer (I) is a stronger acid than (II).

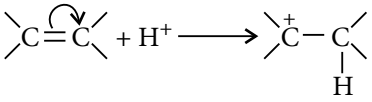
Electromeric Effect

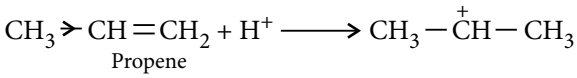
- This is a temporary effect operating in unsaturated compounds only at the demand of a nearby reagent and as soon as this attacking reagent is removed, the original condition is restored.
- It involves the complete transfer of π-electrons of multiple bond, because π-bonds are loosely held and easily polarisable.



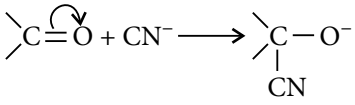
Thus the complete transfer of shared pair of π-electrons of a multiple bond to the more electronegative atom of the bonded atoms due to the requirement of an attacking reagent is called electromeric effect (*E*-effect).

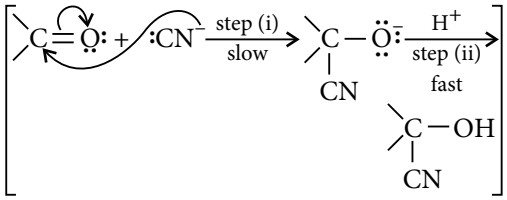
- When the transfer of π-electrons takes place towards the attacking reagent (electrophile), the effect is called +*E*-effect.





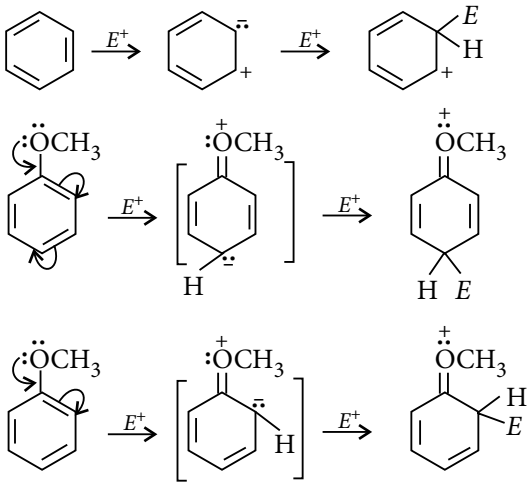
- When the transfer of electrons takes place away from the attacking reagent, the effect is called –*E*-effect.





- When the *I*- and *E*-effect occur together in a molecule, they may be assisting or opposing each other. When they are opposing, the *E*-effect generally dominates over *I*-effect.
- **Applications :**
  - Electrophilic addition reactions of unsaturated compounds involve the polarisation of the carbon- carbon double bond in the presence of attacking electrophiles like H^+.

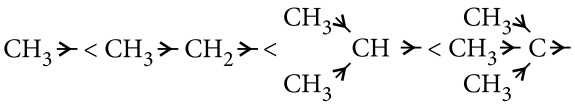
- Nucleophilic addition reactions of carbonyl compounds involve polarisation through electromeric effect of the carbon-oxygen double bond in the presence of a nucleophile.
- Electrophilic substitution reactions of benzenoids involve polarisation through electromeric effect of the benzene ring when an electrophile (E^+) approaches them.



Hyperconjugation

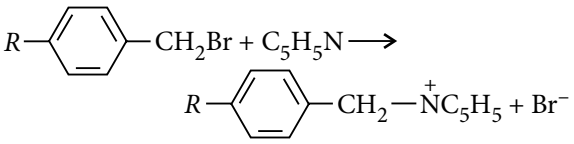
- Hyperconjugation is the stabilizing interaction that results from the interaction of the electrons in a sigma bond (usually C – H or C – C) with an adjacent empty or partially filled non-bonding π-orbital or antibonding *p*-orbital to give an extended molecular orbital that increases the stability of the system.
- Conjugated dienes like 1,3-butadiene have been found to be more stable than simple alkenes like 1-butene. This has been explained in terms of delocalization of π-electrons.
- Besides conjugation even alkyl groups bearing hydrogen on the carbon that is attached to doubly bonded carbon atoms tend to increase the stability of alkenes.
- Propene ($CH_3 - CH = CH_2$) for example has been found to be more stable than ethene ($CH_2 = CH_2$) by about 11 kJ/mole.

  This can be explained in terms of delocalization of electrons which takes place by the overlapping between a π-orbital of carbon and a σ-orbital of the H of methyl group. As a result of this overlapping, each pair of electrons does not just bind together two atoms *i.e.*, the doubly bonded carbons or the carbon and hydrogen but all the four atoms. This delocalization which involves σ-bond orbitals also, is referred to as hyperconjugation or σ, π-conjugation.
- The concept of hyperconjugation was developed on the basis of discovery of anomalous electron releasing pattern of alkyl groups. The inductive (+*I*) effect of alkyl groups is normally in the following order :

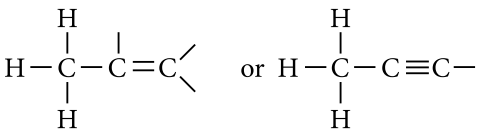


- Baker and Nathan observed that when alkyl groups are attached to an unsaturated system, the order of inductive effect is disturbed and in some cases actually reversed. For example, the rate of reaction of *p*-alkyl benzyl bromide with pyridine was contrary to what was expected from the order of the inductive effect of the substituent alkyl group *i.e.*, rate of the above reaction follows the order :

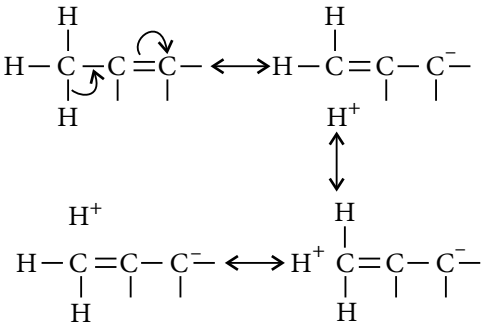
  methyl > ethyl > isopropyl > *tert* butyl.



  This effect is known as Baker-Nathan effect. It is a permanent effect. In fact hyperconjugation is an extension of resonance.
- Resonance effect involves delocalization of π-electrons of two or more conjugated double bonds while hyperconjugation involves delocalization of σ-electrons. Hyperconjugation can be described as double bond - no bond resonance.
- Conjugation between the σ-electrons of single bond and π-electrons of multiple bond *i.e.*, σ,π-conjugation is known as hyperconjugation.
- **Hyperconjugation is of two types :**
  - **Sacrificial hyperconjugation :** The essential condition is the attachment of alkyl group to double bond or triple bond.

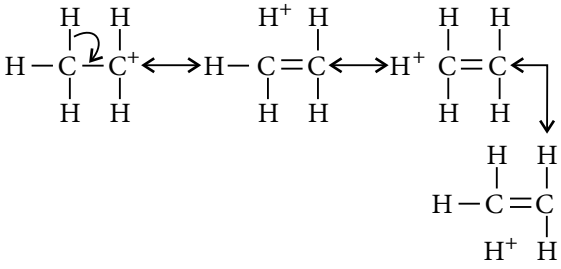


    Carbon atom of alkyl group attached to double bond must contain atleast one hydrogen atom in hyperconjugation.

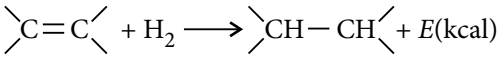


It involves a sort of sacrifice of bond.

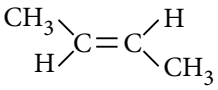
- **Isovalent hyperconjugation :** This kind of hyperconjugation involves no sacrifice of bonds. Ethyl radicals have the same number of real bonds as the classical structure.



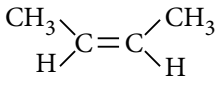
- **Significance of hyperconjugation :**
  - **Heat of hydrogenation :**



Lesser the heat of hydrogenation, lesser is the internal energy and more is the stability of the system. Hyperconjugation decreases the heat of hydrogenation.

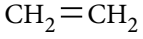


trans-2-Butene
ΔH = 27.6 kcal/mol



cis-2-Butene
ΔH = 28.6 kcal/mol

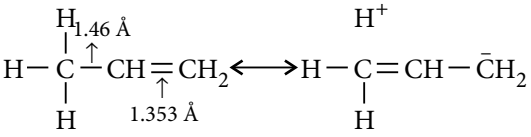
Propene
ΔH = 30.1 kcal/mol



Ethylene
ΔH = 32.8 kcal/mol

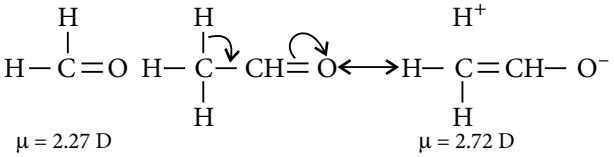
cis-2-Butene is less stable than *trans*-2-butene due to repulsion between two bulkier groups close to each other.

  - **Stability of carbonium ions :** Greater the number of H-atoms present on the carbon atoms α to unsaturation, more are the resonating forms possible due to hyperconjugation and thus greater is the stability of carbonium ion.
  - **Bond length :** Hyperconjugation, like conjugation and resonance, also affects bond length.

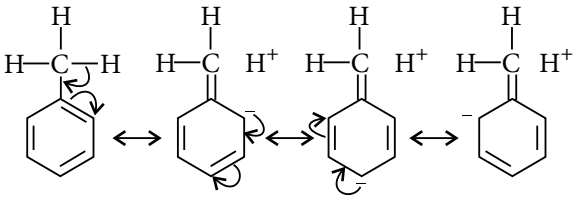


Bond length in propene is 1.46 Å in contrast to normal 1.54 Å (in propane). It is due to the partial double bond character acquired and hence a little shorter.

  - **Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

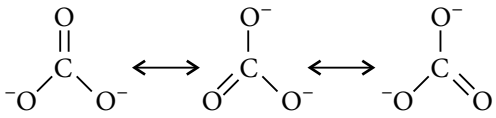


  - *Ortho-para* directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyperconjugation.



Resonance Effect

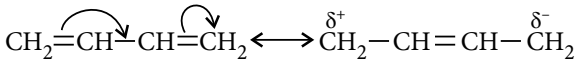
- The concept of resonance pertains to the fact that there are a number of compounds which could be assigned two or more Lewis structures, differing only in the relative position of electrons. However, the actual properties of the substance are not represented by any of these structures but by a structure which is a 'blend' or 'hybrid' of various contributing structures. For example, the following three Lewis structures can be written for the carbonate anion.



These structures reveal that the carbonate anion contains two carbon-oxygen single bonds and one carbon-oxygen double bond but neither of these predictions is consistent with the observation that

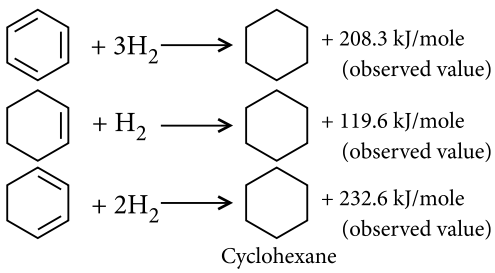
all the C – O bonds in carbonate anion are of equal length (1.30 Å).

- If single and double bonds are present alternatively in a molecule (in case of conjugated system) then π-electrons are delocalized *i.e.*, electrons can flow from one part to another part of the system. This flow of electrons is due to resonance and it results in polarity of the system.



This effect is called mesomeric effect and is transmitted throughout the chain. This is also a permanent effect like inductive effect.

- **Resonance effect is of two types :**
  - **+*M* or +*R* effect :** The groups which donate the electrons to the double bond or to a conjugated system are said to have +*M* effect or +*R* effect. *e.g.*, – OH, – O*R*, – NH*R*, – NR_2, – Cl, – Br, –I, etc.
  - **–*M* or –*R* effect :** The groups which withdraw the electrons from the double bond or from a conjugated system towards themselves are said to have —*M* effect or –*R* effect. *e.g.*, $\rangle C{=}O$, —CHO, —CN, —NO_2, —COO*R*, etc.
- The term mesomerism is used synonymously with resonance. Molecule showing resonance involves overlap of *p*-orbitals in both directions and there is participation of each *p*-electron in more than one bond. In other words resonance and delocalization are used often in the same sense.
- **Resonance energy :** Resonance hybrid is more stable than any single discrete structure. This can be explained in terms of energy of stabilization known as resonance energy. The resonance energy is calculated from the difference between the theoretical and experimental heats of hydrogenation of the compound.



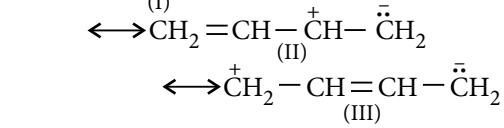
The main postulates of resonance theory are :

- Resonating structures should differ only in the position of electrons, not in the position of atoms.
- Resonating structures should have the same number of unpaired electrons.
- Greater the stability of a contributing structure, greater is its contribution to the hybrid.
- Smaller the difference in the energy contents (or stabilities) of the contributing structures, greater is the resonance energy of that hybrid.
- The polar contributing structures involving distinct charges, are less stable (and hence less important) than those which do not involve any charges.
- Greater the number of contributing structures, greater is the stability.
- Larger the number of bonds in a contributing structure, greater is the stability of that structure.
- All the atoms should have octet of electrons except hydrogen which has duplet. The resonance structures which violate octet rule, should not be considered.
- The skeleton of the molecule should be planar in conjugated system which is necessary in order to achieve maximum overlap of *p*-orbitals. Any structural feature that destroys coplanarity of the conjugated system inhibits resonance. This inhibition is known as steric inhibition of resonance.
- In resonance hybrid, the bond lengths are different from those in the contributing structures.
- No. of π-bonds ∝ No. of contributing structures ∝ Resonance energy ∝ Stability

- **Applications :**
  - By knowing the resonating structures, we can get bond order in a given ion as :

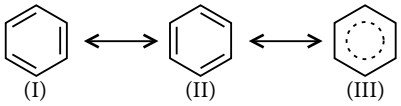
$$\text{Bond order} = \frac{\text{Total no. of bonds}}{\text{Total no. of resonating structures}}$$

  - Resonating structures of dienes :



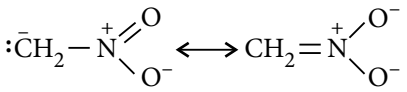
The contributing structures (II) and (III) provide a satisfactory explanation for 1,2 and 1,4 addition and stability of conjugated dienes over simple alkenes.

- All the carbon–carbon bonds in benzene are equivalent, (there are no true single and double bonds as expected from the contributing structures) having exactly the same length (139 pm).



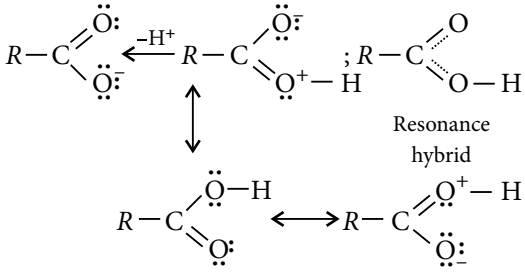
Besides this, benzene has large resonance energy (151 kJ/mole) and hence stability is expected for this system.

- The lower pK_a values of nitromethane and acetyl acetone are simply because of resonance stabilisation of their conjugate bases.

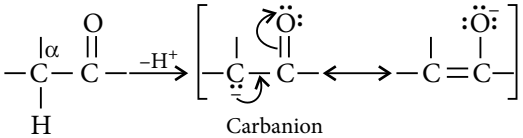


Resonance stabilised conjugate base of nitromethane

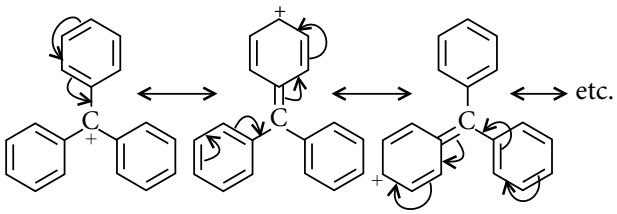
- The acidity of carboxyl group is primarily because of ease of proton release and later, the conjugate base carboxylate ion, is stabilised by forming two equivalent contributing forms.



- **Acidity of α-hydrogen in carbonyl compounds :** This is due to the resonance stabilisation of resulting carbanions.



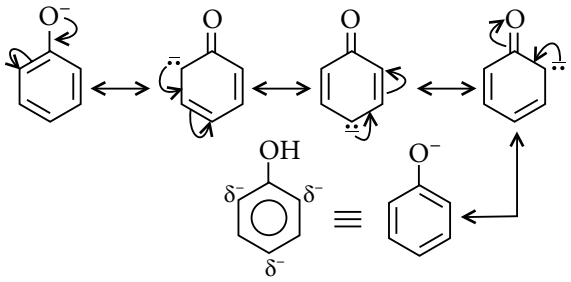
- **Stability of triphenylmethyl cation :** Its stability is due to the extensive delocalisation of the positive charge.



- **Acidic character of phenols :** Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution.

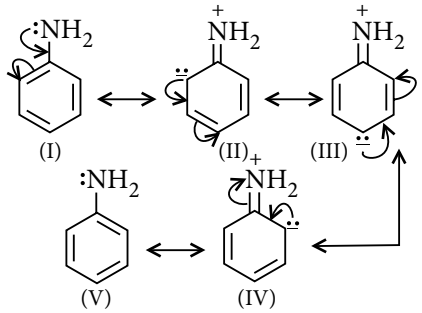
Phenoxide ion

Phenoxide ion is stable due to resonance.



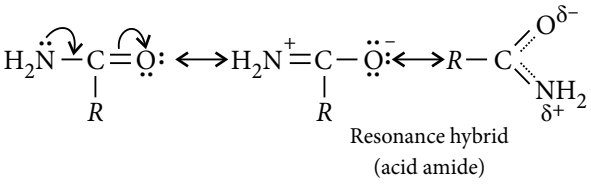
The negative charge is spread throughout the benzene ring. This charge delocalization is a stabilizing factor in the phenoxide ion and increased acidity of phenol. No resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is localized on oxygen atom. Thus, alcohols are less acidic than phenols.

- **Effect of substituents on the acidity of phenols :** Presence of electron attracting group ($-NO_2$, $-NR_3^+$, $-CN$, $-CHO$, $-COOH$) on the benzene ring increases the acidity of phenol. Nitro group in nitro phenol if present in ortho and para positions would stabilise the phenoxide ion by dispersal of negative charge through resonance or mesomeric effect, to a greater extent and will be more acidic than phenol.
- **Base weakening effect of amines :** In case of aryl amines, resonance effect comes into play. Aniline, for example is a resonance hybrid of structures I to V.

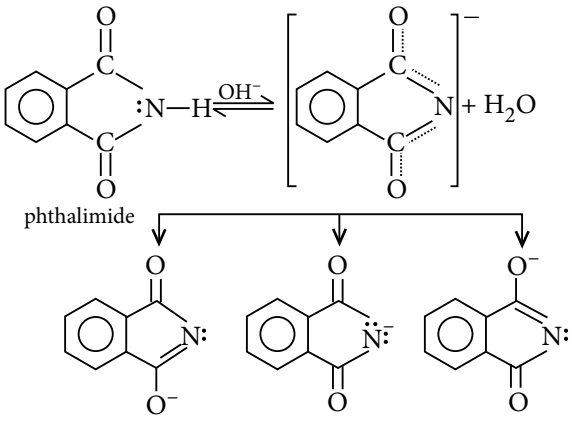


Aniline is far less weaker base than aliphatic amines, primarily due to its resonance stabilization and secondarily, the anilinium cation loses the stabilization because of protonation. Electron withdrawing groups like $—NO_2$ when present at *o*- or *p*- position with respect to aniline will further weaken the basic character of aniline. *e.g.*, *p*-nitroaniline is a weaker base than aniline. The extra base weakening effect when nitro is in the *o*-position, is primarily due to short distance (*–I* effect assisting the resonance), and secondarily, because of direct interaction (both steric and hydrogen bonding). Thus, *o*-nitroaniline is such a weak base that its salts are largely hydrolysed in aqueous solution.

In contrast to amines, the amides and imides are much less basic because of the resonance stabilisation of the molecules. It is practically difficult to protonate an imide.



Resonance hybrid
(acid amide)



phthalimide

Resonance Effect *vs* Inductive Effect

Both are permanent effects, but there are significant differences between the two which are outlined below :

- Resonance effect operates in unsaturated (preferably one with a conjugated system) compounds while inductive effect operates in compounds containing σ-bonds. In other words, π-electrons are involved in resonance effect but only σ-electrons are involved in inductive effect.
- Inductive effect is distance dependent (its intensity decreases sharply with distance from the crucial atom in the chain) while resonance effect is not.
- Resonance effect involves delocalisation of electrons, but there is no such delocalisation in compounds showing inductive effect.

Directive or Orientation Effect

The substituent already present on the benzene ring directs the incoming substituent to occupy, (2 or 6) *ortho*, *meta* (3 or 5) or *para* (4) position. This direction depends on the nature of the first substituent and is called directive or the orientation effect.

- **Class I : (*o*, *p*-directing groups) :** $–R$(alkyl), –OH, –SH, $–NH_2$, $–OR$, $–NHR$, $–NR_2$, $–NHCOR$, –Cl, –Br, –I, $–CH_2Cl$, $–CH_2OH$, $–CH_2NH_2$, $–CH_2CN$, $–CH_2COOH$, $–CH = CH_2$, $–CH = CHCOOH$, $–C_6H_5$, $–N = N$, –NC, etc.
- **Class II : (*m*-directing groups) :** $–SO_3H$, $–NO_2$, –CHO, –COOH, –CN, $–NH_3Cl$, $–SO_2Cl$, –COCl, $–COOR$, $–COR$, $–CCl_3$, $–\overset{+}{N}H_3$, $–\overset{+}{N}H_2R$, $–\overset{+}{N}R_3$, , etc.

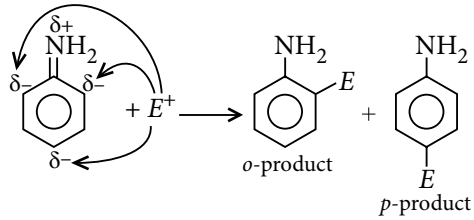
  All *ortho*, *para*-directing substituents possess atleast one non-bonding electron pair on the 'key atom'

  $–\ddot{Cl}:$, $–\ddot{Br}:$, $–\ddot{O}H$, $–\ddot{O}CH_3$, $–\ddot{N}H_2$

  The only exception to the above rule is the methyl or alkyl group.
- **Theory of directive effects :** The resonance theory clearly explains why certain substituents are *ortho-para* directing, while others are *meta* directing.

- ***ortho-para* Directing :** The non-bonding electron pair of the key atom of the substituent is delocalized on the ring by interaction with the π-system due to which *ortho* and *para* positions attain greater electron density and the electrophile (E^+) would naturally attack at these electron rich centres forming *ortho* and *para* isomers. *ortho-para* Directing groups activate the benzene ring towards electrophilic substitution while *meta* directing groups deactivate the benzene nucleus towards electrophilic substitution.

  –F, –Cl, –Br and –I (halogens) are exceptions to the above rule. These groups are *o*-, *p*- directing but deactivate the ring.

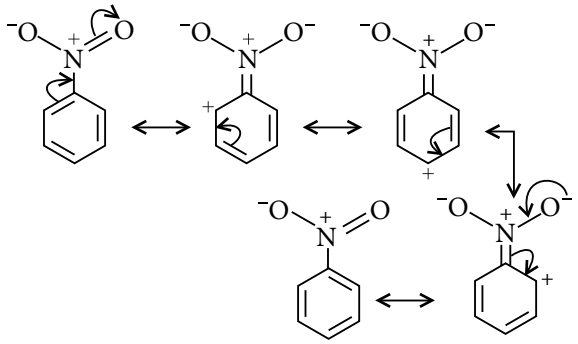


- ***meta*-Directing :** The substituent withdraws electrons from *ortho* and *para*-positions. Thus, *m*-position becomes a point of relatively high electron density and further substitution by electrophile occurs at *meta*-position.

  Any substituent or group which releases (donates) electrons into the ring (*i.e.,* *o*, *p*-directing) activates the benzene ring for further substitution. The substituent which withdraws electrons (*m*-directing) from the ring deactivates the benzene ring for further substitution.

  In case of halogen *–I* effect predominates resonance effect.

  $-NO_2$ group is *meta*-directing (electron withdrawing), its mechanism can be explained as



  All *meta*-directing groups have either a partial positive charge or a full positive charge on the atom directly attached to the ring.

Introduction of a Third Substituent into Benzene Ring

The position occupied by a third substituent group entering the benzene ring is mainly decided by the nature of the two groups already present on the benzene ring.

- When both groups are (*o*-, *p*-directing) then the directive influence of each group is in the following order :

  $O^- > NR_2, > NH_2 > OH > OMe >$

  $NHCOCH_3 > CH_3 > X$

  The new group enters *p*-position preferably with respect to more powerful group.

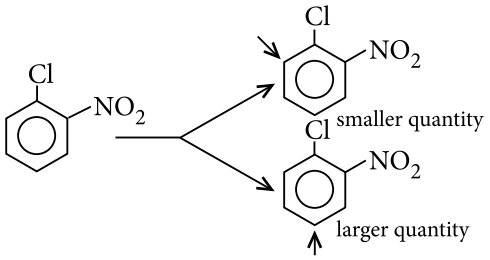
  In case the *p*-position is blocked, the third group enters the position *ortho* to the more powerful group.

- When both groups are *meta*-directing the third group is accomodated according to the following order :

  $Me_3N^+ > NO_2 > CN > SO_3H > CHO > COMe > COOH$

  The new substituent occupies *meta*-position with respect to the more powerful group.

- When two groups exert different directive influence then *o*, *p*-directors take precedence.



- In case the influence of two groups reinforce each other, the third group is attached to one position, only.

ADVANCED CHEMISTRY BLOC

(IDEAL SOLUTIONS)

Mukul C. Ray, Odisha

Ideal Solution

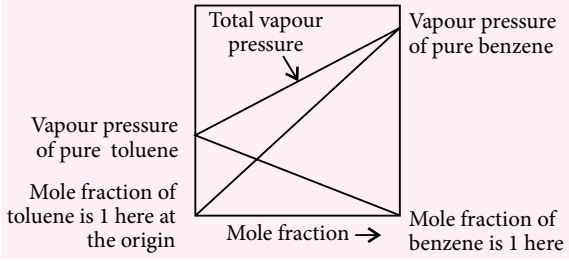
An ideal solution is defined as a mixture in which the molecules of different species are indistinguishable. Unlike the ideal gas, they exert forces on each other. When these forces are same for all molecules, independent of species, then a solution is said to be ideal. In an ideal solution, the equilibrium between the solution concentration and the vapour phase partial pressure is described by Raoult's law for each component. This means each component follows Raoult's law in the entire range of concentrations. Note that ideally dilute solution is different than ideal solution. In the ideally dilute solution the solute follows Henry's law and solvent the Raoult's law but in the ideal solution both solvent and the solute follow Raoult's law. Ideally dilute solutions are easily found but ideal solutions are only nearly achieved. Substances with similar molecules usually form nearly ideal solutions. Toluene–benzene, ethylene dibromide–propylene dibromide, carbon tetrachloride–silicon tetrachloride, ethyl chloride–ethyl bromide are such examples.

Mathematically,

$$P_T = p^\circ_A x_A + p^\circ_B x_B$$

where the terms p°_A and p°_B are vapour pressures of the pure components '*A*' and '*B*' respectively. x_A and x_B are the mole fractions of components '*A*' and '*B*' in the liquid phase.

Consider a specific example of a solution of benzene and toluene.



The partial vapour pressure of benzene and toluene in a solution. The graph is not to scale but showing at least benzene is more volatile than toluene.

Thermodynamics of Ideal Solution

For an ideal solution, state variables such as *V*, *U*, *H* and *G* are obtained by adding the corresponding contributions of solvent '*A*' and solute '*B*'.

For example, the volume

$$V_{AB} = n_A V_{m,A} + n_B V_{m,B}$$

where $V_{m,A}$ and $V_{m,B}$ are the molar volumes of '*A*' and '*B*' respectively. For an ideal solution at constant *T* and *P*, the mixing quantities behave as follows :

$$\Delta_{mix}G = RT\sum_i n_i \ln x_i,\ \Delta_{mix}S = -R\sum_i n_i \ln x_i$$

And, $\Delta_{mix}V = 0, \Delta_{mix}H = 0$

The value of $\Delta_{mix}G$ is actually the value of *G* for the solution relative to the pure component. Physically $\Delta_{mix}H = 0$ means no heat is lost or gained by the system when two components of the solution interact. In other words, the strength of forces between '*A*' and '*B*' is almost of same strength as *A*-*A* and *B*-*B*.

Total Vapour Pressure versus Composition

Since total mole fraction of both the components taken together is one, the expression for the total vapour pressure can be written as :

$$P_T = p^\circ_B + (p^\circ_A - p^\circ_B)x_A$$

So the plot of the total vapour pressure against mole fraction of component '*A*' in liquid phase gives a straight line graph with intercept as the vapour pressure of pure component '*B*' and slope of the line as $(p^\circ_A - p^\circ_B)$.

It is very natural that during the evaporation, the more volatile component will pass into the vapour phase preferentially. Therefore, the vapour phase composition is different than the liquid phase composition and the vapour phase composition can be obtained with the help of Dalton's law of partial pressure.

$$y_A = \frac{p_A}{P_T} = \frac{x_A p_A^\circ}{p_B^\circ + (p_A^\circ - p_B^\circ)x_A}$$

To express the total vapour pressure in terms of composition of vapour phase, the above equation is rearranged to get an expression of x_A in terms of y_A.

$$x_A = \frac{y_A p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A}$$

Substituting this value of x_A in the expression of total pressure,

$$P_T = p_B^\circ + (p_A^\circ - p_B^\circ)x_A$$

or, $$P_T = p_B^\circ + (p_A^\circ - p_B^\circ) \times \frac{y_A p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A}$$

or $$P_T = \frac{p_B^\circ p_A^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A}$$

So assuming $p_A^\circ < p_B^\circ$,

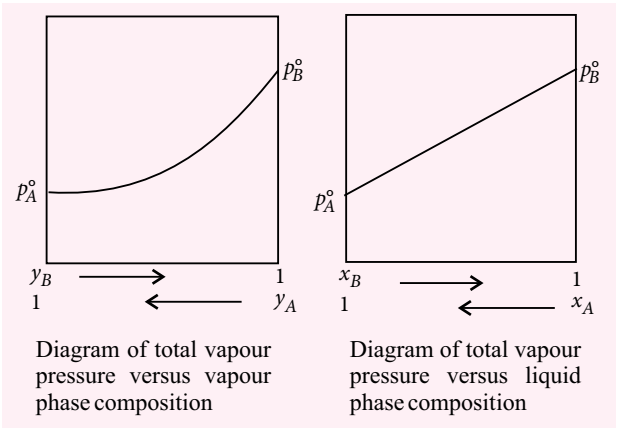
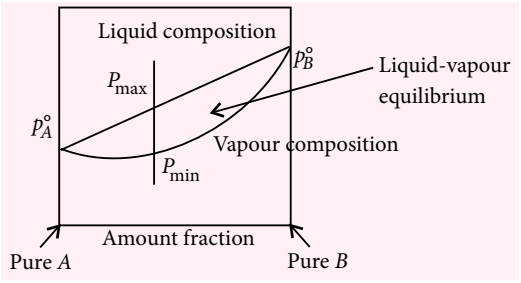


Diagram of total vapour pressure versus vapour phase composition

Diagram of total vapour pressure versus liquid phase composition

These plots straightaway follow from the mathematical equations showing the dependence of total vapour pressure on vapour phase composition (left diagram) and on liquid phase composition (right one). When the two diagrams are superimposed, diagram as shown is obtained. Here the x-axis is showing amount fraction. For linear line it is the liquid phase composition (line is called liquidus or the bubble point line) and for the other one - it is the vapour phase composition (line is called vapourous or the dew point line). Note that all these diagrams are at constant temperature.

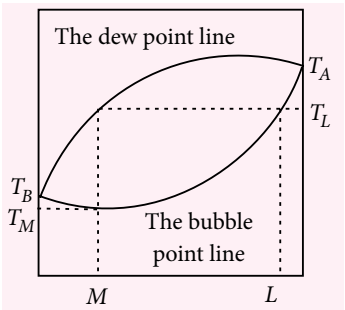


From the diagram, the conclusions are :

- If the system pressure (may be the pressure created by the piston of the cylinder in which the liquid is kept) is more than maximum pressure, only liquid phase exists.
- If the system pressure is less than minimum pressure, only vapour phase exists.
- If the system pressure is in between, then a liquid-vapour equilibrium is observed.

Boiling Point versus Composition

For an ideal solution, the graph of boiling point versus amount fraction is shown. The liquid having higher vapour pressure has the lower boiling point. Since 'B' is more volatile than 'A', the boiling point of the former is less. One more notable point is the position of lines and their curve like nature. None of the line is a straight line and it immediately follows from their mathematical equations. Also the vapourous curve called as 'the dew point line' is on the top and the liquidus line called 'the bubble point line' is at the bottom.



The significance of the diagram can be easily realized. For a solution whose composition is shown by point 'L', the boiling point would be 'T_L'. The vapours coming out would have composition shown by point 'M'. When these vapours are condensed, the resulting liquid would have boiling point 'T_M'. By repeating this process again and again, the more volatile component 'B' can be obtained from vapours and less one from the residual liquid.

AIPMT

SOLVED PAPER 2015

Hurray!! We are happy to inform our readers that out of the 45 questions asked in AIPMT 2015, many questions were either exactly same or of similar type from the **MTG Books.** Hurray!!

Here, the references of few are given :

Exam Q. No.	MTG Book	Q. No.	P. No.
1	27 years AIPMT	48	26
2	27 years AIPMT	20	184
4	27 years AIPMT	28	140
5	NCERT Fingertips	56	337
9	27 years AIPMT	2	162
11	Objective Chemistry	2	148
12	27 years AIPMT	43	123

Exam Q. No.	MTG Book	Q. No.	P. No.
18	27 years AIPMT	4	113
19	NCERT Fingertips	42	126
30	AIPMT Guide	195	278
31	27 years AIPMT	32	25
32	27 years AIPMT	15	88
37	Objective Chemistry	1	871
43	27 years AIPMT	11	9

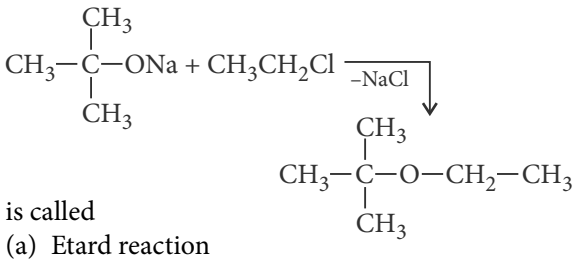
and more such questions .....

1. Which of the following pairs of ions are isoelectronic and isostructural?

(a) SO_3^{2-}, NO_3^- (b) ClO_3^-, SO_3^{2-}

(c) CO_3^{2-}, SO_3^{2-} (d) ClO_3^-, CO_3^{2-}

2. The reaction,



is called

(a) Etard reaction

(b) Gattermann-Koch reaction

(c) Williamson synthesis

(d) Williamson continuous etherification process.

3. The boiling point of 0.2 mol kg^{-1} solution of *X* in water is greater than equimolal solution of *Y* in water. Which one of the following statements is true in this case?

(a) Molecular mass of *X* is less than the molecular mass of *Y*.

(b) *Y* is undergoing dissociation in water while *X* undergoes no change.

(c) *X* is undergoing dissociation in water.

(d) Molecular mass of *X* is greater than the molecular mass of *Y*.

4. The activation energy of a reaction can be determined from the slope of which of the following graphs?

(a) $\ln k$ *vs.* $\frac{1}{T}$ (b) $\frac{T}{\ln k}$ *vs.* $\frac{1}{T}$

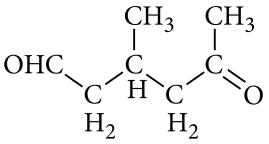
(c) $\ln k$ *vs.* T (d) $\frac{\ln k}{T}$ *vs.* T

5. Biodegradable polymer which can be produced from glycine and aminocaproic acid is

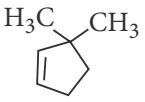
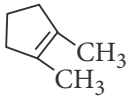
(a) buna-N (b) nylon 6,6

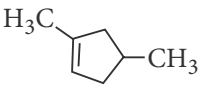
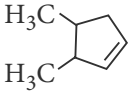
(c) nylon 2-nylon 6 (d) PHBV.

6. A single compound of the structure,



is obtainable from ozonolysis of which of the following cyclic compounds?

(a)  (b) 

(c)  (d) 

7. The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4?
(a) AgBr (b) Ag_2CrO_4
(c) AgI (d) AgCl

8. The correct bond order in the following species is
(a) $O_2^+ < O_2^- < O_2^{2+}$ (b) $O_2^- < O_2^+ < O_2^{2+}$
(c) $O_2^{2+} < O_2^+ < O_2^-$ (d) $O_2^{2+} < O_2^- < O_2^+$

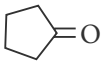
9. Magnetic moment 2.84 B.M. is given by :
(At. nos. Ni = 28, Ti = 22, Cr = 24, Co = 27)
(a) Cr^{2+} (b) Co^{2+}
(c) Ni^{2+} (d) Ti^{3+}

10. The number of *d*-electrons in Fe^{2+} (Z = 26) is not equal to the number of electrons in which one of the following?
(a) *d*-electrons in Fe ($Z = 26$)
(b) *p*-electrons in Ne ($Z = 10$)
(c) *s*-electrons in Mg ($Z = 12$)
(d) *p*-electrons in Cl ($Z = 17$)

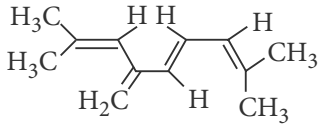
11. Which of the following options represents the correct bond order?
(a) $O_2^- > O_2 < O_2^+$ (b) $O_2^- < O_2 > O_2^+$
(c) $O_2^- > O_2 > O_2^+$ (d) $O_2^- < O_2 < O_2^+$

12. Which one of the following electrolytes has the same value of van't Hoff factor (*i*) as that of $Al_2(SO_4)_3$ (if all are 100% ionised)?
(a) $Al(NO_3)_3$ (b) $K_4[Fe(CN)_6]$
(c) K_2SO_4 (d) $K_3[Fe(CN)_6]$

13. "Metals are usually not found as nitrates in their ores."
Out of the following two (I and II) reasons which is/are true for the above observation?
I. Metal nitrates are highly unstable.
II. Metal nitrates are highly soluble in water.
(a) I is false but II is true.
(b) I is true but II is false.
(c) I and II are true.
(d) I and II are false.

14. Treatment of cyclopentanone  with methyl lithium gives which of the following species?
(a) Cyclopentanonyl radical
(b) Cyclopentanonyl biradical
(c) Cyclopentanonyl anion
(d) Cyclopentanonyl cation

15. The function of "Sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of this pump?
(a) K^+ (b) Fe^{2+}
(c) Ca^{2+} (d) Mg^{2+}

16. The total number of π-bond electrons in the following structure is

(a) 12 (b) 16
(c) 4 (d) 8

17. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is
(a) second
(b) more than zero but less than first
(c) zero (d) first.

18. A given metal crystallises out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom?
(a) 80 pm (b) 108 pm
(c) 40 pm (d) 127 pm

19. Which of the following statements is correct for a reversible process in a state of equilibrium?
(a) $\Delta G^\circ = -2.30\ RT \log K$
(b) $\Delta G^\circ = 2.30\ RT \log K$
(c) $\Delta G = -2.30\ RT \log K$
(d) $\Delta G = 2.30\ RT \log K$

20. A mixture of gases contains H_2 and O_2 gases in the ratio of 1 : 4 (*w*/*w*). What is the molar ratio of the two gases in the mixture?
(a) 16 : 1 (b) 2 : 1
(c) 1 : 4 (d) 4 : 1

21. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C?
(a) $CoCl_3 \cdot 5NH_3$ (b) $CoCl_3 \cdot 6NH_3$
(c) $CoCl_3 \cdot 3NH_3$ (d) $CoCl_3 \cdot 4NH_3$

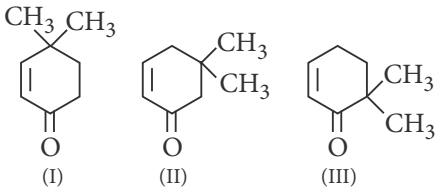
22. If the value of equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain
(a) mostly products
(b) similar amounts of reactants and products
(c) all reactants (d) mostly reactants.

23. Which of the following species contains equal number of σ- and π-bonds?
(a) $(CN)_2$ (b) $CH_2(CN)_2$
(c) HCO_3^- (d) XeO_4

24. Which of these statements about $[Co(CN)_6]^{3-}$ is true?
(a) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin configuration.
(b) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration.
(c) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.
(d) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.

25. An organic compound 'X' having molecular formula $C_5H_{10}O$ yields phenylhydrazone and gives negative response to the iodoform test and Tollens' test. It produces *n*-pentane on reduction. 'X' could be
(a) 3-pentanone (b) *n*-amyl alcohol
(c) pentanal (d) 2-pentanone.

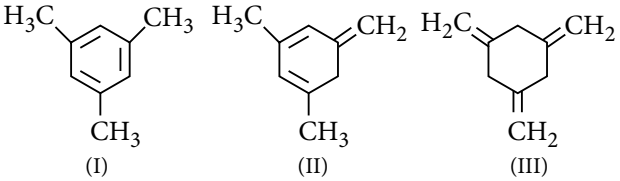
26. Given :



Which of the given compounds can exhibit tautomerism?
(a) II and III (b) I, II and III
(c) I and II (d) I and III

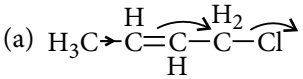
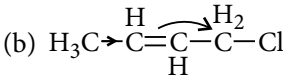
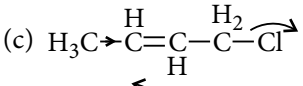
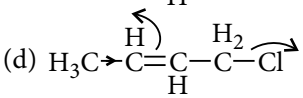
27. Bithional is generally added to the soaps as an additive to function as a/an
(a) buffering agent (b) antiseptic
(c) softener (d) dryer.

28. Given :



The enthalpy of hydrogenation of these compounds will be in the order as
(a) II > III > I (b) II > I > III
(c) I > II > III (d) III > II > I

29. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place?

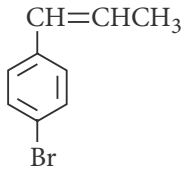
(a) 
(b) 
(c) 
(d) 

30. Solubility of the alkaline earth metal sulphates in water decreases in the sequence
(a) Sr > Ca > Mg > Ba (b) Ba > Mg > Sr > Ca
(c) Mg > Ca > Sr > Ba (d) Ca > Sr > Ba > Mg

31. Maximum bond angle at nitrogen is present in which of the following?
(a) NO_2^+ (b) NO_3^-
(c) NO_2 (d) NO_2^-

32. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is
(a) 16.76 (b) 15.76
(c) 17.36 (d) 18.20

33. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other?
(a) Is soluble in water.
(b) Is used as a food preservative.
(c) Forms 'acid-rain'.
(d) Is a reducing agent.

34. The reaction of $C_6H_5CH{=}CHCH_3$ with HBr produces
(a) $C_6H_5CH_2CH_2CH_2Br$ (b) 

(c) $C_6H_5\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$ (d) $C_6H_5CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

35. Which of the following processes does not involve oxidation of iron?
(a) Formation of $Fe(CO)_5$ from Fe.
(b) Liberation of H_2 from steam by iron at high temperature.
(c) Rusting of iron sheets.
(d) Decolourisation of blue $CuSO_4$ solution by iron.

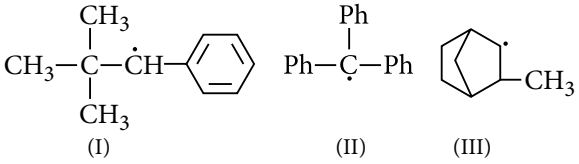
36. Which of them is not equal to zero for an ideal solution?
(a) ΔV_{mix} (b) $\Delta P = P_{observed} - P_{Raoult}$
(c) ΔH_{mix} (d) ΔS_{mix}

37. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers)
(a) Zr(40) and Hf(72) (b) Zr(40) and Ta(73)
(c) Ti(22) and Zr(40) (d) Zr(40) and Nb(41)

38. Which property of colloidal solution is independent of charge on the colloidal particles?
(a) Electro-osmosis (b) Tyndall effect
(c) Coagulation (d) Electrophoresis

39. The electrolytic reduction of nitrobenzene in strongly acidic medium produces
(a) azobenzene (b) aniline
(c) *p*-aminophenol (d) azoxybenzene.

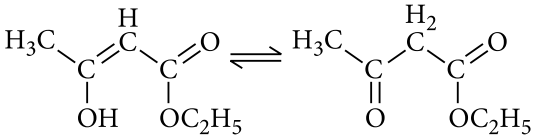
40. Consider the following compounds :



(I) (II) (III)

Hyperconjugation occurs in
(a) III only (b) I and III
(c) I only (d) II only.

41. The enolic form of ethyl acetoacetate as shown below has



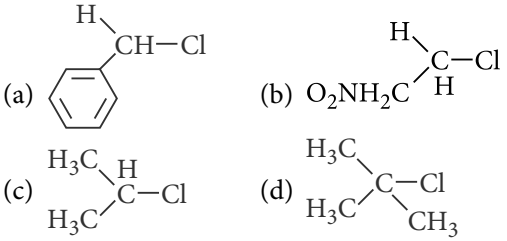
(a) 9 sigma bonds and 2 pi-bonds
(b) 9 sigma bonds and 1 pi-bond
(c) 18 sigma bonds and 2 pi-bonds
(d) 16 sigma bonds and 1 pi-bond.

42. The species Ar, K^+ and Ca^{2+} contain the same number of electrons. In which order do their radii increase?
(a) $Ca^{2+} < K^+ < Ar$ (b) $K^+ < Ar < Ca^{2+}$
(c) $Ar < K^+ < Ca^{2+}$ (d) $Ca^{2+} < Ar < K^+$

43. The angular momentum of electron in '*d*' orbital is equal to
(a) $2\sqrt{3}\,\hbar$ (b) $0\ \hbar$
(c) $\sqrt{6}\,\hbar$ (d) $\sqrt{2}\,\hbar$

44. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as
(a) dynamo (b) Ni-Cd cell
(c) fuel cell (d) electrolytic cell.

45. In which of the following compounds, the C—Cl bond ionisation shall give most stable carbonium ion?



SOLUTIONS

1. **(b) :**

Species	Hybridisation	Shape	No. of e^-s
SO_3^{2-}	sp^3	Pyramidal	42
ClO_3^-	sp^3	Pyramidal	42
CO_3^{2-}	sp^2	Triangular planar	32
NO_3^-	sp^2	Triangular planar	32

2. **(c) :** Williamson synthesis is the best method for the preparation of ethers.

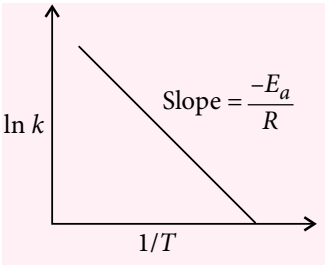
3. **(c) :** $\Delta T_b = iK_b\,m$
For equimolal solutions, elevation in boiling point will be higher if solution undergoes dissociation *i.e.*, $i > 1$.

4. **(a) :** According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

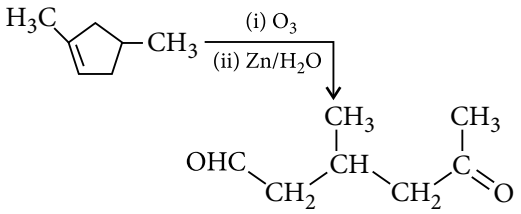
$$\ln k = \ln A - \frac{E_a}{RT}$$

Hence, if ln k is plotted against $1/T$, slope of the line will be $-\frac{E_a}{R}$.



5. **(c) :** $nH_2N{-}CH_2{-}COOH + nH_2N{-}(CH_2)_5{-}COOH$
Glycine Aminocaproic acid
$\longrightarrow$ $\text{-(HN}{-}CH_2{-}CO{-}NH{-}(CH_2)_5{-}CO\text{-)}_n$
Nylon 2-nylon 6

6. **(c) :**



7. (b) :

Salt	K_{sp}	Solubility
Ag_2CrO_4	$1.1 \times 10^{-12} = 4s^3$	$s = \sqrt[3]{\frac{K_{sp}}{4}} = 0.65 \times 10^{-4}$
AgCl	$1.8 \times 10^{-10} = s^2$	$s = \sqrt{K_{sp}} = 1.34 \times 10^{-5}$
AgBr	$5 \times 10^{-13} = s^2$	$s = \sqrt{K_{sp}} = 0.71 \times 10^{-6}$
AgI	$8.3 \times 10^{-17} = s^2$	$s = \sqrt{K_{sp}} = 0.9 \times 10^{-8}$

$\because$ Solubility of Ag_2CrO_4 is highest thus, it will be precipitated at last.

8. (b) : O_2^- O_2 O_2^+ O_2^{2+}
B.O. : 1.5 2.0 2.5 3.0

9. (c) : Magnetic moment (μ) = $\sqrt{n(n+2)}$
2.84 B.M. corresponds to 2 unpaired electrons.
Cr^{2+} – $3d^4$, 4 unpaired electrons
Co^{2+} – $3d^7$, 3 unpaired electrons
Ni^{2+} – $3d^8$, 2 unpaired electrons
Ti^{3+} – $3d^1$, 1 unpaired electron

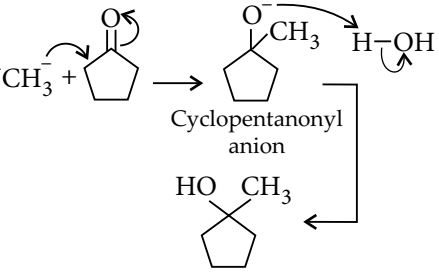
10. (d) : Number of *d*-electrons is Fe^{2+} = 6
Number of *p*-electrons in Cl = 11

11. (d) : $O_2^- < O_2 < O_2^+$
B.O. : 1.5 2.0 2.5

12. (b) : $Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$, $i = 5$
$Al(NO_3)_3 \longrightarrow Al^{3+} + 3NO_3^-$, $i = 4$
$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$, $i = 5$
$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$, $i = 3$
$K_3[Fe(CN)_6] \longrightarrow 3K^+ + [Fe(CN)_6]^{3-}$, $i = 4$

13. (a) : All nitrates are soluble in water and are quite stable as they do not decompose easily on heating.

14. (c) :



15. (a)

16. (d) : There are four double bonds. Hence, no. of π-electrons = $2 \times 4 = 8$.

17. (d) : Half life period of a first order reaction is independent of initial concentration,

$$t_{1/2} = \frac{0.693}{k}$$

18. (d) : $Z = 4$, *i.e.,* structure is *fcc*.

Hence, $r = \frac{a}{2\sqrt{2}} = \frac{361}{2\sqrt{2}} = 127.65 \text{ pm} \approx 127 \text{ pm}$

19. (a)

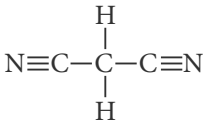
20. (d) : Number of moles of $H_2 = \frac{1}{2}$

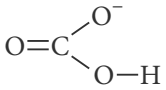
Number of moles of $O_2 = \frac{4}{32}$

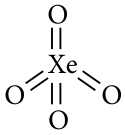
Hence, molar ratio = $\frac{1}{2} : \frac{4}{32} = 4 : 1$

21. (c) : For octahedral complexes, coordination number is 6.
Hence, $CoCl_3 \cdot 3NH_3$ *i.e.,* $[Co(NH_3)_3Cl_3]$ will not ionise and will not give test for Cl^- ion with silver nitrate.

22. (a) : The value of *K* is high which means reaction proceeds almost to completion *i.e.,* the system will contain mostly products.

23. (d) : $CH_2(CN)_2$,  (6 σ + 4 π)

HCO_3^-,  (4 σ + 1 π)

XeO_4,  (4 σ + 4 π)

$(CN)_2$, $N \equiv C - C \equiv N$ (3 σ + 4 π)

24. (c) : $[Co(CN)_6]^{3-}$, oxidation no. of Co = +3
$Co^{3+} = 3d^6$
As CN^- is a strong field ligand, so all electrons will be paired up and complex will be low spin complex.

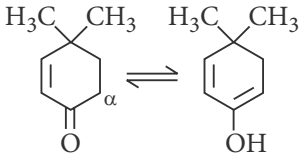
25. (a) : Compound '*X*' yields phenylhydrazone

$\Rightarrow -\overset{\overset{O}{\|}}{C}-$ group.

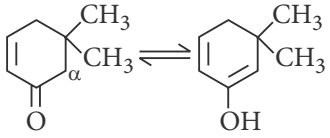
Negative iodoform test $\Rightarrow CH_3-\overset{\overset{O}{\|}}{C}-$ group is absent.
Negative Tollens' test $\Rightarrow$ ketone
Hence, the compound is 3-pentanone.

$$\underset{\text{3-Pentanone}\ (C_5H_{10}O)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3} \xrightarrow{\text{Reduction}} \underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

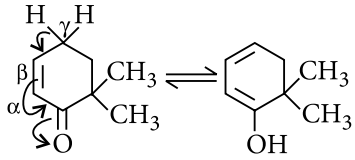
26. (b) : In keto-enol tautomerism,

(I) 

here, α-H participates.

(II) 

here, α-H participates.

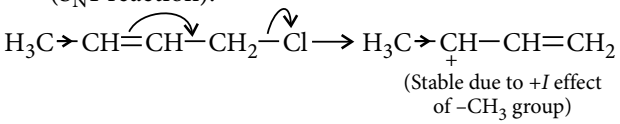
(III) 

here, γ-H participates (*p*-tautomerism).

27. (b)

28. (d) : Enthalpy of hydrogenation is inversely proportional to the stability of alkenes.
Stability of alkenes : I > II > III
Enthalpy of hydrogenation : I < II < III

29. (a) : Nucleophile will attack a stable carbocation (S_N1 reaction).



30. (c) : Solubility of alkaline earth metal sulphates decreases down the group because hydration energy decreases.

31. (a) :

Species	NO_3^-	NO_2	NO_2^-	NO_2^+
Hybridisation	sp^2	sp^2	sp^2	sp (linear)
Bond angle	120°	134°	115°	180°

So, NO_2^+ has maximum bond angle.

32. (a) : Mass of organic compound = 0.25 g

Experimental values,	At STP,
V_1 = 40 mL	V_2 = ?
T_1 = 300 K	T_2 = 273 K
P_1 = 725 – 25 = 700 mm	P_2 = 760 mm

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$$

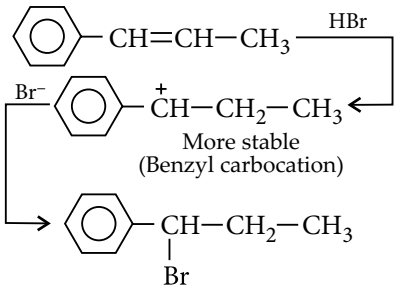
$$V_2=\frac{P_1V_1T_2}{T_1P_2}=\frac{700\times40\times273}{300\times760}=33.52\text{ mL}$$

22400 mL of N_2 at STP weighs = 28 g

$$\therefore\quad 33.52\text{ mL of }N_2\text{ at STP weighs} = \frac{28\times33.52}{22400}$$
$$= 0.0419\text{ g}$$

$$\%\text{ of N}=\frac{\text{Mass of nitrogen at STP}}{\text{Mass of organic compound taken}}\times100$$
$$=\frac{0.0419}{0.25}\times100=16.76\%$$

33. (b) : NO_2 is not used as a food preservative.

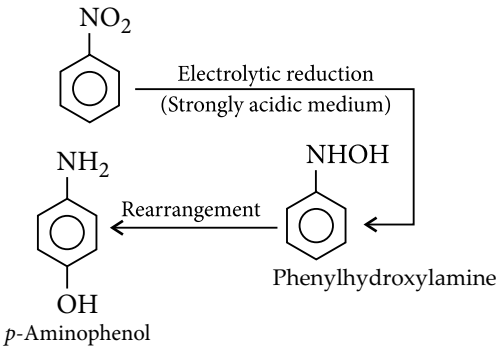
34. (c) : 

35. (a) : Oxidation number of Fe in $Fe(CO)_5$ is zero.

36. (d) : For an ideal solution, $\Delta S_{mix} > 0$ while ΔH_{mix}; ΔV_{mix} and $\Delta P = 0$.

37. (a) : Zr and Hf have nearly same radii due to lanthanoid contraction.

38. (b) : Tyndall effect is scattering of light by colloidal particles which is independent of charge on them.

39. (c) : 

40. (a) : Hyperconjugation can occur only in compound III as it has α-hydrogen atoms.

41. (c)

42. (a) : In case of isoelectronic species, radius decreases with increase in nuclear charge.

43. (c) : Angular momentum $=\sqrt{l(l+1)}\,\hbar$

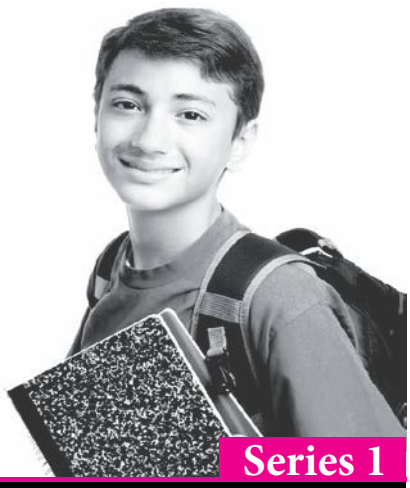
For *d* orbital, $l = 2$

Angular momentum $=\sqrt{2(2+1)}\,\hbar=\sqrt{6}\,\hbar$

44. (c)

45. (d) : $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}}$ is most stable due to hyper-conjugation.

ACE YOUR WAY CBSE XII



Series 1

CHAPTERWISE PRACTICE PAPER : THE SOLID STATE | SOLUTIONS

Time Allowed : 3 hours | Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Which type of solids are called giant molecules?

2. Why are soda water and soft drink bottles sealed under high pressure?

3. Why is Frenkel defect not found in pure alkali metal halides?

4. What type of solution is formed when ethanol is mixed with water?

5. What happens when ferrimagnetic Fe_3O_4 is heated at 850 K?

6. When lime (CaO) is dissolved in water, solution becomes quite hot. What is the effect of temperature on the solubility of CaO in water?

7. Why is $FeO_{(s)}$ not formed in stoichiometric composition?

8. Define vapour pressure. What happens to the vapour pressure when
(i) a volatile solute is dissolved in the liquid?
(ii) a non-volatile solute is dissolved in the liquid?

9. The compound CuCl has ZnS structure and the edge length of the unit cell is 500 pm. Calculate its density. [Atomic mass of Cu = 63 u, Cl = 35.5 u]

OR

In a compound AX, the radius of A^+ ion is 95 pm and that of X^- ion is 181 pm. Predict the crystal structure of AX and write the coordination number of each of the ion.

10. 4% NaOH solution (mass/volume) and 6% urea solution (mass/volume) are equimolar but not isotonic. Why?

11. Assign reasons for the following :
(i) Phosphorus doped silicon is a semiconductor.
(ii) Schottky defect lowers the density of a solid.
(iii) Some of the very old glass objects appear slightly milky instead of being transparent.

12. **(i)** What is meant by van't Hoff factor?
(ii) The osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27°C. Calculate the van't Hoff factor. (R = 0.082 L atm K^{-1} mol^{-1}) What conclusion do you draw about the molecular state of the solute in the solution?

13. Explain the following terms with suitable examples :

(i) Antiferromagnetism

(ii) Frenkel defect

(iii) Forbidden zone

14. What weight of the non-volatile urea ($NH_2—CO—NH_2$) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

15. (i) What is the difference between 13-15 and 12-16 compounds?

(ii) In corrundum, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-third of the octahedral voids. What is the formula of corrundum?

16. Based on solute-solvent interactions, arrange the following in order of increasing solubility in *n*-octane and explain.

Cyclohexane, KCl, CH_3OH, CH_3CN

17. What is a semiconductor? Describe two main types of semiconductors giving example and their distinctive features.

18. (i) Why is the elevation in boiling point of water different in the following solutions?

(a) 0.1 molar NaCl solution

(b) 0.1 molar sugar solution.

(ii) What advantage does osmotic pressure method have over the elevation in boiling point method for determining molecular masses?

19. (i) What general name is given to binary mixtures which show deviations from Raoult's law and whose components cannot be separated by fractional distillation?

(ii) Why is it not possible to obtain pure ethanol by fractional distillation?

(iii) How many types of such mixtures are there?

OR

(i) (a) State Henry's law for solubility of a gas in liquid and explain its significance.

(b) At the same temperature hydrogen is more soluble in water than helium. Which of them will have a higher value of K_H and why?

(ii) Mention two applications of Henry's law.

20. Distinguish between the following pairs of terms :

(i) Hexagonal close packing and cubic close packing

(ii) Crystal lattice and unit cell

(iii) Tetrahedral void and octahedral void.

21. (i) Non-stoichiometric cuprous oxide, Cu_2O can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a *p*-type semiconductor?

(ii) Classify each of the following as a *p*-type or *n*-type semiconductor :

(a) Ge doped with In

(b) B doped with Si

22. The molal freezing point depression constant of benzene (C_6H_6) is 4.90 K kg mol^{-1}. Selenium exists as a polymer of the type Se_x . When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than for pure benzene. Deduce the molecular formula of selenium. (At. mass of Se = 78.8 g mol^{-1}).

23. Ms. Abha, a public health worker, always tells people in the villages not to cook food in open *kadahi*. She insists on using pressure cooker or covered pans for cooking as it will preserve the nutritional value of the food and cook food faster.

(i) What values are displayed by Ms. Abha?

(ii) What is the reason for fast cooking in pressure cooker?

(iii) What is molal elevation constant?

(iv) How is it related to elevation in boiling point?

24. (i) Aluminium crystallises in a cubic close packed structure. Radius of atom in the metal is 125 pm.

(a) What is the length of the side of the unit cell?

(b) How many unit cells are there in 1 cm^3 of aluminium?

(c) How many atoms are there in 1 unit cell?

(ii) Define the following terms in relation to crystalline solids :

(a) Lattice point

(b) Coordination number

Give one example in each case.

OR

(i) Explain anisotropic and isotropic properties of solids.

(ii) Calculate the packing efficiency of a crystal for a face centred cubic lattice.

25. (i) Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1.0 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of *A* and *B*.

(ii) What happens when RBCs are placed in
(a) 1% NaCl solution?
(b) Pure water?

OR

(i) Illustrate elevation in boiling point with the help of vapour pressure-temperature curve of a solution. Show that elevation in boiling point is a colligative property.

(ii) Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g of octane to reduce its vapour pressure to 80%.

26. (i) Calculate the number of atoms per unit cell in a
(a) face centred cubic structure
(b) body centred cubic structure.

(ii) If the radius of the octahedral void is *r* and radius of the atoms in close packing is *R*, derive relation between *r* and *R*.

OR

(i) Explain
(a) The basis of similarities and differences between metallic and ionic crystals.
(b) Ionic crystals are hard and brittle.

(ii) What are F-centres?

(iii) Zinc oxide on heating becomes yellow. Why?

SOLUTIONS

1. Covalent (network) solids are called giant molecules.

2. Soda water and soft drink bottles are sealed under high pressure because solubility of CO_2 is high at higher pressure.

3. Frenkel defect is not found in pure alkali metal halides because alkali metal ions cannot fit into the interstitial sites.

4. When ethanol is mixed with water, non-ideal solution showing positive deviations from ideal behaviour is formed.

5. When ferrimagnetic Fe_3O_4 is heated at 850 K it loses ferrimagnetism and becomes paramagnetic due to greater alignment of spins is one direction on heating.

6. Dissolution of CaO in water is an exothermic process *i.e.*, heat is evolved. According to Le Chateliers principle, increase in temperature decreases solubility while decrease in temperature increases solubility.

7. In FeO crystals, some Fe^{2+} ions are replaced by Fe^{3+} ions. To balance net charge, three Fe^{2+} ions are replaced by two Fe^{3+} ions. Eventually, there would be less amount of metal as compared to stoichiometric composition.

8. The pressure exerted by gas molecules on its liquid layer at equilibrium is called vapour pressure.
(i) When a volatile liquid is added to another liquid then the resultant vapour pressure may increase, decrease or may remain same depending on the strength of solute-solvent interaction.
(ii) Net vapour pressure decreases when a non-volatile solute is added to the liquid.

9. Given, structure = *fcc*, a = 500 pm

For CuCl, $M = 63 + 35.5 = 98.5$ g mol^{-1}, d = ?

For *fcc*, $Z = 4$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$

or $d = \dfrac{4 \times 98.5 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1} \times (500)^3 \times 10^{-30} \text{ cm}^3}$

$= 5.234 \text{ g cm}^{-3}$

OR

Given, r_{A^+} = 95 pm, r_{X^-} = 181 pm, structure = ?

C.No. = ?

$$\text{Radius ratio} = \frac{r_{A^+}}{r_{X^-}} = \frac{95 \text{ pm}}{181 \text{ pm}} = 0.524$$

Radius ratio lies between 0.414 to 0.732 hence, cations are in the octahedral voids of *ccp* of anions. Hence, structure is *fcc*, C.No. = 6.

10. Both the solutions, 4% NaOH (*W*/*V*) and 6% urea (*W*/*V*) have same concentration (1 M) but these are not isotonic because NaOH undergoes dissociation in solution. Therefore, number of particles in NaOH solution is more than that in urea solution.

11. (i) When silicon (having four valence electrons) is doped with phosphorus (having five valence electrons), phosphorus occupies some of the lattice sites in the crystal. Four out of five electrons are used in the formation of covalent bonds with neighbouring atoms. The fifth extra electron becomes delocalised and moves in the crystal lattice making it a semiconductor.

(ii) In Schottky defect, equal number of cations and anions are missing from their normal position in the crystal lattice so, it decreases the density of the crystal.

(iii) This is because due to heating during the day and cooling at night *i.e.*, annealing over a number of years, glass acquires some crystalline character.

12. (i) van't Hoff factor is the ratio of the normal molecular mass to the observed molecular mass or the ratio of the observed colligative property to the normal colligative property.

(ii) $\pi = iCRT$

or, $0.70 = i \times 0.0103 \times 0.082 \times (27 + 273)$

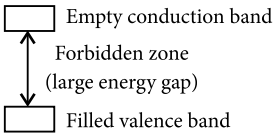
or, $i = \dfrac{0.70}{0.0103 \times 0.082 \times 300} = 2.76$

Since $i > 1$, solute molecules are dissociated in the solution.

13. (i) Substances which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called antiferromagnetic substances, *e.g.*, MnO. It is due to the presence of equal number of magnetic moments in the opposite directions.

(ii) Frenkel defect arises when smaller ions (usually cations) in the lattice occupy interstitial sites leaving lattice sites vacant. This defect is generally found in ionic crystals where anion is much larger in size than the cation, *e.g.*, AgBr, ZnS, etc. Due to this defect density does not change, electrical conductivity increases to a small extent and there is no change in overall chemical composition of the crystal.

(iii) The energy gap between the fully filled valence band and the empty conduction band is called forbidden zone.



14. Given :

$p^\circ = 100$ $\qquad w_A = 100$ g

$p_s = 75$ $\qquad w_B = ?$

For urea, $M_B = 60$ g mol^{-1}

For water, $M_A = 18$ g mol^{-1}

$$\frac{p^\circ - p_s}{p_s} = \frac{n_B}{n_A} = \frac{w_B / M_B}{w_A / M_A} \quad \therefore \quad \frac{25}{75} = \frac{w_B / 60}{100 / 18}$$

or $\quad w_B = 111$ g

Molality of the solution

$$= \frac{111 \text{ g}}{60 \text{ g mol}^{-1}} \times \frac{1}{100 \text{ g}} \times 1000 \text{ g kg}^{-1}$$

$= 18.5$ mol kg^{-1} or 18.5 m

15. (i) Group 13-15 compounds *viz.* AlP, GaAs, etc. have large covalent character whereas Group 12-16 compounds *viz.* ZnS, CdS, HgTe, etc. do not possess covalent bonds but have sufficient ionic character.

(ii) Let the number of oxide ions in the packing be N.

The number of octahedral voids $= N$

Therefore, Al^{3+} ions $= \dfrac{2}{3} \times N = \dfrac{2N}{3}$

$\therefore$ Ratio of $Al^{3+} : O^{2-} = \dfrac{2N}{3} : N = 2 : 3$

Hence, formula of corrundum is Al_2O_3.

16. Cyclohexane and *n*-octane both are non-polar. Hence, they mix completely in all proportions.

KCl is an ionic compound while *n*-octane is non-polar. Hence, KCl will not dissolve at all in *n*-octane.

CH_3OH and CH_3CN, both are polar but CH_3CN is less polar than CH_3OH. As the solvent is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Thus, the order of solubility will be :

KCl < CH_3OH < CH_3CN < Cyclohexane

17. The solids which have conductivities between 10^{-6} to 10^4 ohm^{-1} m^{-1} are called semiconductors. *e.g.*, germanium and silicon.

Concerned about your performance in Class XII Boards?

Well, fear no more, help is at hand.....

To excel, studying in right direction is more important than studying hard. Which is why we created the Excel Series. These books – for Physics, Chemistry, Biology & Mathematics – have been put together totally keeping in mind the prescribed syllabus and the pattern of CBSE's Board examinations, so that students prepare and practice with just the right study material to excel in board exams.

Did you know nearly all questions in CBSE's 2015 Board Examination were a part of our Excel books? That too fully solved ?!

HIGHLIGHTS:

- Comprehensive theory strictly based on NCERT, complemented with illustrations, activities and solutions of NCERT questions
- Practice questions & Model Test Papers for Board Exams
- Value based questions
- Previous years' CBSE Board Examination Papers (Solved)

*Scan now with your smartphone or tablet**

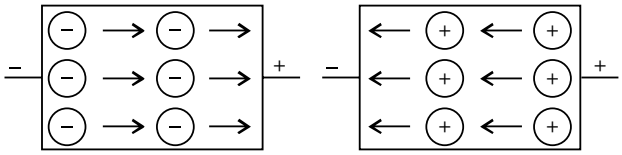
Visit **www.mtg.in** for latest offers and to buy online!

mtG Learning Media

Available at all leading book shops throughout the country.
For more information or for help in placing your order:
Call 0124-4951200 or email: info@mtg.in
**Application to read QR codes required*

The two main types of semiconductors are as follows :

(i) ***n*-type semiconductor :** When a silicon crystal is doped with atoms of group-15 elements, such as P, As, Sb or Bi then only four of the five valence electrons of each impurity atom participate in forming covalent bonds and fifth electron is almost free to conduct electricity. Such type of semiconductors are called *n*-type semiconductors as increase in conductivity is due to negatively charged electrons.



n-type semiconductor *p*-type semiconductor

(ii) ***p*-type semiconductor :** When a silicon crystal is doped with atoms of group-13 elements, such as B, Al, Ga or In, each impurity atom forms only three covalent bonds with the host atom. The place where the fourth electron is missing is called a hole which moves through the crystal like a positive charge and hence increases its conductivity. Such type of semiconductors are called *p*-type semiconductors.

18 (i) ΔT_b is different in the two cases because NaCl dissociates into Na^+ and Cl^- ions in the solution while sugar does not dissociate. Therefore, number of particles in case of NaCl is higher than that in sugar.

(ii) Advantages of osmotic pressure method over elevation in boiling point method are as follows :

(a) Osmotic pressure measurement occurs at room temperature.

(b) This method uses molarities instead of molalities.

(c) Value of osmotic pressure is large even for dilute solutions.

(d) It is more suitable for biomolecules which are not stable at higher temperature.

19. (i) Azeotropic mixtures.

(ii) It is not possible to obtain pure ethanol by fractional distillation because a mixture of 95.6% ethanol with 4.4% water forms an azeotrope *i.e.*, a constant boiling mixture.

(iii) There are two types of such mixtures :

(a) Minimum boiling azeotropes : They show large positive deviations from Raoult's law (as ethanol-water system).

(b) Maximum boiling azeotropes : They show large negative deviations from Raoult's law (as nitric acid-water system).

OR

(i) (a) Henry's law states that the solubility of a gas in liquid at a constant temperature is directly proportional to the partial pressure of the gas in equilibrium with the liquid.

Mathematically, $p = K_H.x$

where p is the pressure of the gas above the solution and x is the mole fraction of the gas in the solution and K_H is Henry's constant.

(b) K_H is a function of the nature of the gas. Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid.

As helium is less soluble in water, so it will have a higher value of K_H than hydrogen.

(ii) (a) In the production of beverages.

(b) In deep sea diving

20. (i) Hexagonal close packing has *ABAB*..... type arrangement. *i.e.*, each third layer is parallel to the first whereas in cubic close packing, arrangement is *ABCABCABC*....type in which each fourth layer is parallel to the first.

(ii) Crystal lattice is the arrangement of lattice points in three dimensional space whereas unit cell is the smallest repeating unit which represents arrangement of lattice points in a crystal lattice.

(iii) A void surrounded by four atoms whose centres when joined form tetrahedron is called tetrahedral void whereas a void surrounded by six atoms whose centres when joined form an octahedron is called octahedral void.

Number of tetrahedral voids = 2 × Number of atoms forming *ccp*

Number of octahedral voids = Number of atoms forming *ccp*

21. (i) Copper to oxygen ratio is less than 2:1 in Cu_2O. This shows that some Cu^+ ions have been replaced by Cu^{2+} ions. To maintain electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion and hence a hole will be created which will be responsible for conduction. Thus this substance is a *p*-type semiconductor.

(ii) (a) Ge is group-14 element (4 valence electrons) and In is group-13 element (3 valence electrons). Hence a hole is created and it is a *p*-type semiconductor.

(b) B is group-13 element (3 valence electrons) and Si is group-14 element (4 valence electrons). Hence, due to presence of a free electron it is a *n*-type semiconductor.

22. Given $K_f = 4.90$ K kg mol^{-1}

$w_B = 3.26$ g

$w_A = 226$ g

$\Delta T_f = 0.112°C$

Atomic mass of Se = 78.8 g mol^{-1}

$$M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f} = \frac{4.90 \times 3.26 \times 1000}{226 \times 0.112}$$

or $M_B = 631$ g mol^{-1}

Number of atoms of Se in a molecule $= \frac{631}{78.8} = 8$

$\therefore$ Molecular formula of selenium is Se_8.

23. (i) Ms. Abha showed social values of saving energy and fuel as well as concern towards the health of villagers.

(ii) In pressure cooker, pressure is high and water boils at higher temperature. Hence more heat is available for cooking the material.

(iii) Molal elevation constant may be defined as the elevation in boiling point when molality of the solution is unity.

(iv) $\Delta T_b = K_b \times m$

24. (i) (a) For *fcc* (or *ccp*), $a = 2\sqrt{2}r = 2 \times 1.414 \times 125$ pm
$= 354$ pm

(b) $a = 354$ pm $= 3.54 \times 10^{-8}$ cm

Volume of one unit cell $= a^3 = (3.54 \times 10^{-8}\text{ cm})^3$
$= 4.44 \times 10^{-23}$ cm^3

Number of unit cells

$$= \frac{\text{Total volume}}{\text{Volume of one unit cell}}$$

$$= \frac{1\text{ cm}^3}{4.44 \times 10^{-23}\text{ cm}^3} = 2.25 \times 10^{22}$$

(c) 1 unit cell has four atoms of aluminium.

(ii) (a) The constituent particles of a crystalline solids are denoted by points. These are called lattice points. Lattice points may be atoms, molecules or ions.

(b) The number of nearest neighbours of any constituent particle in a crystal lattice is called its coordination number. The coordination number of an atom in the *bcc* structure is 8.

OR

(i) Some of the physical properties of crystalline solids like electrical conductivity, refractive index etc. show different values when measured along different directions in the same crystal. This is called anisotropic property of the crystal.

Since, the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction.

In case of amorphous substances, these properties are identical in all directions. This property is called isotropy.

(ii) Edge length = a

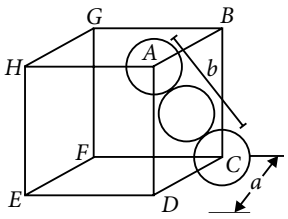
Face diagonal $= b = AC$

In ΔABC

$AC^2 = BC^2 + AB^2$

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}\,a$



If radius of the spherical atom is r then

$$b = \sqrt{2}\,a = 4r$$

$$\therefore \quad r = \frac{a}{2\sqrt{2}}$$

Volume of the four spherical atoms of radius r in the unit cell is

$$\frac{4}{3}\pi r^3 \times 4 = \frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3 \times 4 = \frac{\pi a^3}{3\sqrt{2}}$$

Volume of the cube $= a^3$

Packing efficiency $=$

$$\frac{\text{Volume of one spherical atom in unit cell}}{\text{Volume of the cube}}$$

$$\therefore \quad \text{Packing efficiency} = \frac{\pi a^3}{3\sqrt{2} \times a^3}$$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

25. (i) Given, $w_2 = 1$ g

$w_1 = 20$ g

$\Delta T_{f(AB_2)} = 2.3$ K

$\Delta T_{f(AB_4)} = 1.3$ K

$K_f = 5.1$ K kg mol^{-1}

Applying the formula, $M_2 = \frac{1000 \times K_f \times w_2}{w_1 \times \Delta T_f}$

$$M_{(AB_2)} = \frac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87 \text{ g mol}^{-1}$$

$$M_{(AB_4)} = \frac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15 \text{ g mol}^{-1}$$

Suppose atomic masses of A and B are 'a' and 'b' respectively then

Molar mass of $AB_2 = a + 2b = 110.87$ g mol^{-1} ...(i)

Molar mass of $AB_4 = a + 4b = 196.15$ g mol^{-1} ...(ii)

Eqn. (ii) - Eqn. (i) gives

$2b = 85.28$ or $b = 42.64$

Substituting in eqn. (i) we get

$a + 2 \times 42.64 = 110.87$ or $a = 25.59$

Thus atomic mass of $A = 25.59$ u

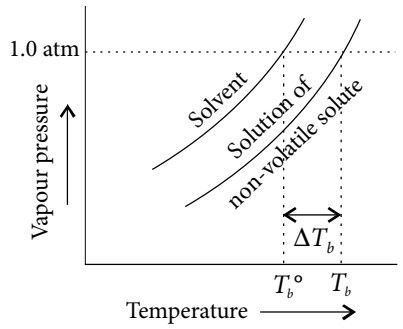
Atomic mass of $B = 42.64$ u

(ii) (a) 1% NaCl solution is hypertonic, hence RBCs will shrink due to plasmolysis.

(b) Pure water is hypotonic hence RBCs will burst due to osmosis.

OR

(i)



Change of vapour pressure of a solvent and solution of non-volatile solute with temperature.

Elevation in boiling point is a colligative property as it depends only on number of moles of solute particles dissolved in 1000 g of the solvent and not upon the nature of the solute *i.e.*

$$\Delta T_b \propto m$$

(ii) Number of moles of solute $= \frac{w}{40}$ mol

Let $p^\circ = 100$ then $p_s = 80$

$\therefore \quad \Delta p = 20$

Number of moles of solvent (octane)

$$= \frac{114 \text{ g}}{114 \text{ g mol}^{-1}} = 1 \text{ mol}$$

[Molar mass of $C_8H_{18} = 114$ g mol^{-1}]

Now, $\frac{\Delta p}{p^\circ} = x_2$

$$\therefore \quad \frac{20}{100} = \frac{w/40}{w/40 + 1}$$

$$0.2\left(\frac{w}{40} + 1\right) = \frac{w}{40}$$

$\Rightarrow \quad w = 10$ g

26. (i) (a) Number of atoms in a unit cell of *fcc* structure : This type of unit cell has 8 atoms on the corners and 6 atoms on the face centres.

Contribution by atoms on the corners

$$= \frac{1}{8} \times 8 = 1$$

Contribution by atoms on the face centres

$$= \frac{1}{2} \times 6 = 3$$

$\therefore$ Total number of atoms per unit cell

$$= 3 + 1 = 4$$

(b) Number of atoms in a unit cell of *bcc* structure : This type of unit cell has 8 atoms on the corners and one atom within the body.

Contribution by 8 atoms present on the corners

$$= \frac{1}{8} \times 8 = 1$$

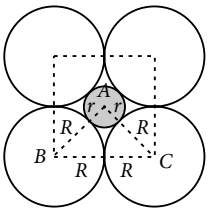
Contribution by atoms present within the body = 1

$\therefore$ Number of atoms present per unit cell

$$= 1 + 1 = 2$$

(ii) Derivation of the relationship between the radius (r) of the octahedral void and the radius (R) of the atoms in close packing :

A sphere fitting into the octahedral void is shown by shaded circle. A sphere above and a sphere below this small (shaded) sphere have not been shown in the figure.



ABC is a right angled triangle. Applying Pythagoras theorem,

$BC^2 = AB^2 + AC^2$

$(2R)^2 = (R + r)^2 + (R + r)^2 = 2(R + r)^2$

$\Rightarrow \frac{(2R)^2}{2} = (R+ r)^2$ or $(\sqrt{2}\,R)^2 = (R + r)^2$

$\Rightarrow \sqrt{2}\,R = R + r$ or $r = \sqrt{2}\,R - R = (\sqrt{2} - 1)R$

$\Rightarrow r = R(1.414 - 1) = 0.414\,R$

OR

(i) (a) Similarities between metallic and ionic crystals :

1. In both ionic and metallic crystals constituent particles are held by electrostatic force of attraction.

2. In both the solids, bonds are non-directional.

3. Both the solids have high melting points.

Differences between metallic and ionic crystals :

1. Ionic crystals are made of cations and anions whereas metallic solids are made of metal ions and sea of electrons.

2. Ionic crystals are insulators in solid state because their ions are not free to move whereas metallic crystals conduct electricity due to the presence of sea of mobile electrons.

3. Ionic crystals are hard and brittle but metallic crystals are hard, malleable and ductile. Some metallic crystals are soft also.

(b) Ionic crystals are hard due to the presence of strong interionic electrostatic forces of attraction.

However, when an ionic solid is subjected to stress, ions of same charge come close together and the repulsive forces between them cause the crystal to break into pieces.

Thus, ionic crystals are hard but brittle.

(ii) Electrons trapped in anionic vacancies are called F-centres as they impart colour to the crystal.

(iii) When ZnO is heated, it loses oxygen and turns yellow due to the following reaction :

$$ZnO \xrightarrow{\Delta} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess Zn^{2+} ions move to interstitial sites and electrons to neighbouring interstitial sites.

These electrons impart colour by absorbing a portion of energy from visible light.

CONCEPT MAP

SOME BASIC CONCEPTS OF CHEMISTRY

Introduction of most fundamental and important tools of chemistry which help in various calculations.

Measurement and uncertainty in measurement

SI Units

- SI system has seven base units pertaining to seven fundamental scientific quantities :

Physical quantity	SI unit
Length (l)	metre (m)
Mass (m)	kilogram (kg)
Time (t)	second (s)
Electric current (I)	ampere (A)
Thermodynamic temperature (T)	kelvin (K)
Amount of substance (n)	mole (mol)
Luminous intensity (I_v)	candela (cd)

- SI system allows the use of prefixes to indicate the multiples or submultiples of a unit :

deci - 10^{-1}	deka - 10^{1}
centi - 10^{-2}	hecto - 10^{2}
milli - 10^{-3}	kilo - 10^{3}
micro - 10^{-6}	mega - 10^{6}
nano - 10^{-9}	giga - 10^{9}
pico - 10^{-12}	tera - 10^{12}

Scientific Notation

- A number is represented as $x \times 10^{n}$
- n is –ve if decimal is moved towards right and n is +ve if it is moved towards left.

Significant Figures

- These are all certain digits with last digit uncertain.
- All non-zero digits are significant.
- Zeros preceding to first non-zero digit are not significant.
- Zeros between two non-zero digits are significant.
- Zeros on the right side of the decimal are significant.

Dimensional Analysis

- Required unit = Given value × conversion factor
- Some useful conversion factors :

Length – $1\,Å = 10^{-8}\,cm = 10^{-10}\,m$
$1\,nm = 10^{-9}\,m$, $1\,pm = 10^{-12}\,m$

Volume – $1\,L = 1000\,mL$
$= 1000\,cm^3 = 1\,dm^3 = 10^{-3}\,m^3$

Pressure – $1\,atm = 760\,mm\,or\,torr$
$= 101325\,Pa$
$1\,bar = 10^{5}\,Nm^{-2} = 10^{5}\,Pa$

Energy – $1\,calorie = 4.184\,J$
$1\,eV = 1.6022 \times 10^{-19}\,J$
$1\,J = 10^{7}\,ergs$

Laws of chemical combinations and Dalton's atomic theory

Law of Conservation of Mass

Matter can neither be created nor destroyed.

Law of Definite Proportions

A given compound always contains exactly the same proportion of elements by weight.

Law of Multiple Proportions

If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

Gay Lussac's Law of Gaseous Volumes

When gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

Avogadro's Law

Equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory

- Matter consists of indivisible atoms.
- All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
- Compounds are formed when atoms of different elements combine in a fixed ratio.
- Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Stoichiometry

- It deals with calculations based upon chemical equations.
- Various steps involved in calculations are :
  - Write balanced chemical equation.
  - Write the relative number of moles or relative masses of reactants and products involved below their formulae.
  - In case of gases write 22.4 L at STP in place of 1 mole.
  - Apply unitary method to make required calculations.

Limiting Reagent

The reactant which gets consumed completely and limits the amount of product formed is called **limiting reagent**.

Mole concept, Masses and Stoichiometry

Masses

- **Atomic mass unit (amu or u) :** Mass exactly equal to $1/12^{th}$ of the mass of an atom of C-12 isotope.
- **Atomic mass of an element :** Average relative mass of its atoms as compared to an atom of C-12.
- **Average atomic mass :** Given for isotopes.
  $= \frac{\Sigma X_i A_i}{\Sigma X_i}$ where X_i = % abundance, A_i = atomic mass
- **Gram atomic mass :** Atomic mass of an element expressed in grams.
- **Molecular mass :** Sum of atomic masses of all the elements present in a molecule.

Mole Concept

Mole : Collection of 6.022×10^{23} particles
In case of
atomic substances :
1 mole = Gram atomic mass = 1 gram atom
$= 6.022 \times 10^{23}$ atoms
molecular substances :
1 mole = Gram molecular mass
= 1 gram molecule
$= 6.022 \times 10^{23}$ molecules
gaseous substances :
1 mole = 22.4 L at STP

Percentage Composition

It shows mass of a constituent in 100 parts of a compound.
Mass % of an element
$= \frac{\text{Mass of that element in the compound}}{\text{Molar mass of the compound}} \times 100$

Empirical Formula

- It is the simplest whole number ratio of different atoms present in a compound.
- Steps to obtain empirical formula :

$\text{Molar ratio} = \frac{\%\text{ age}}{\text{At. mass}}$ → Change to

$\text{Simplest molar ratio} = \frac{\text{Molar ratio}}{\text{Minimum molar ratio}}$ → Change to

Simplest whole number ratio = Simplest ratio × Integer

Write the numbers below the symbols of elements → Empirical formula

Molecular Formula

- It is the formula showing exact number of atoms present in a molecule.
- Molecular formula = n × empirical formula

Reactions in Solutions

- Mass percent (%) $= \frac{w_{solute}}{w_{solution}} \times 100$
- Mole fraction $(x_A) = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$
- Molarity $(M) = \frac{w_2 \times 1000}{M_2 \times V(\text{in mL})}$
- Molality $(m) = \frac{w_2 \times 1000}{M_2 \times w_1(\text{in g})}$

HAVE A LOOK !

- Mass is the quantity of matter contained in the substance and is constant whereas weight varies from place to place.
- Exact numbers have an infinite number of significant figures.
- Molar volume of a gas is 22.7 L at 1 bar and 0°C.
- The number of molecules in 1 mL of a gas at STP is known as **Loschmidt number**.

SOLVED PAPER 2015

Kerala PMT

1. Which one of the following sets of quantum numbers is possible ?
   (a) $n = 3, l = 3, m_l = -3, m_s = +1/2$
   (b) $n = 2, l = 1, m_l = 2, m_s = -1/2$
   (c) $n = 2, l = 0, m_l = 0, m_s = +1/2$
   (d) $n = 1, l = 0, m_l = 0, m_s = 0$
   (e) $n = 3, l = 2, m_l = 3, m_s = -1/2$

2. The mass of $CaCO_3$ required to react completely with 20 mL of 1.0 M HCl as per the reaction,
   $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$ is
   (At. wt : Ca = 40, C = 12, O = 16)
   (a) 1 g (b) 2 g
   (c) 10 g (d) 20 g
   (e) 200 g

3. Which one of the following has maximum number of molecules?
   (a) 16 g of O_2 (b) 16 g of NO_2
   (c) 4 g of N_2 (d) 2 g of H_2
   (e) 32 g of N_2

4. The density of 2.0 M solution of a solute is 1.2 g mL^{-1}. If the molecular mass of the solute is 100 g mol^{-1}, then the molality of the solution is
   (a) 2.0 m (b) 1.2 m
   (c) 1.0 m (d) 0.6 m
   (e) 2.4 m

5. Which of the following sets of molecules contains the same number of lone pairs of electrons in the central atom?
   (a) SO_2, ClF_3, BrF_3 (b) SF_4, NH_3, O_3
   (c) ClF_3, XeF_2, H_2O (d) H_2O, SF_4, NH_3
   (e) NH_3, XeF_2, O_3

6. Which one of the following does not match with respect to the shape of the molecule?
   (a) NH_3 – Trigonal pyramidal
   (b) SF_4 – Tetrahedral
   (c) H_2S – Bent
   (d) ClF_3 – T-shape
   (e) XeF_4 – Square planar

7. Find the pair that has the same bond order with diamagnetic and paramagnetic properties respectively.
   (a) F_2 and O_2 (b) N_2 and O_2^{2-}
   (c) Li_2 and B_2 (d) B_2 and O_2
   (e) He and Ne

8. In which one of the following compounds does the central atom obey the octet rule?
   (a) XeF_4 (b) $XeOF_2$
   (c) SCl_2 (d) $AlCl_3$
   (e) BF_3

9. Equal masses of He, O_2 and SO_2 are taken in a closed container. The ratio of the partial pressures of gases He, O_2 and SO_2 would be
   (a) 1 : 2 : 8 (b) 8 : 16 : 1
   (c) 16 : 8 : 1 (d) 1 : 4 : 16
   (e) 16 : 2 : 1

10. Which one of the following gases has the highest critical temperature?
    (a) Nitrogen (b) Ammonia
    (c) Water vapour (d) Carbon dioxide
    (e) Hydrogen

11. Match the following :

Compound	Magnetic property
(A) NaCl	(i) Ferrimagnetic
(B) MnO	(ii) Paramagnetic
(C) $CrCl_3$	(iii) Ferromagnetic
(D) CrO_2	(iv) Diamagnetic
(E) $MgFe_2O_4$	(v) Antiferromagnetic

(a) (A)–(i), (B)–(iii), (C)–(ii), (D)–(v), (E)–(iv)
(b) (A)–(v), (B)–(ii), (C)–(iii), (D)–(i), (E)–(iv)
(c) (A)–(iii), (B)–(v), (C)–(ii), (D)–(i), (E)–(iv)
(d) (A)–(iv), (B)–(v), (C)–(ii), (D)–(iii), (E)–(i)
(e) (A)–(iv), (B)–(iii), (C)–(v), (D)–(ii), (E)–(i)

12. What would be the IUPAC name for the element with atomic number 120?
(a) Ununbium (b) Unnilbium
(c) Unnilunium (d) Ununtrium
(e) Unbinilium

13. Among Mg, Mg^{2+}, Al and Al^{3+} which will have the largest and the smallest size respectively?
(a) Mg, Al^{3+} (b) Al^{3+}, Mg
(c) Mg^{2+}, Al (d) Al, Mg^{2+}
(e) Mg^{2+}, Al^{3+}

14. How does the electron gain enthalpies vary across a period and down a group?
(a) More positive across a period and less positive down a group.
(b) More negative across a period and less negative down a group.
(c) Less positive across a period and less negative down a group.
(d) More positive across a period and less negative down a group.
(e) Less negative across a period and more negative down a group.

15. The halide of which alkaline earth metal is covalent and soluble in organic solvents?
(a) Be (b) Mg
(c) Ca (d) Sr
(e) Ba

16. The element responsible for the neuromuscular function in the body is
(a) calcium (b) magnesium
(c) potassium (d) sodium
(e) manganese.

17. The salt of an alkali metal gives yellow colour in the flame test. Also its aqueous solution gives an insoluble white precipitate with barium chloride in acid medium. The salt is
(a) NaCl (b) K_2SO_4
(c) Na_2SO_4 (d) Li_2SO_4
(e) $NaNO_3$

18. The oxoacid of phosphorus that reduces silver nitrate into metallic silver is
(a) H_3PO_2 (b) $H_4P_2O_6$
(c) H_3PO_4 (d) $H_4P_2O_7$
(e) $(HPO_3)_n$

19. The compound that is used in nuclear industry as protective shields and control rods is
(a) metal carbonates (b) metal chlorides
(c) metal oxides (d) metal hydroxides
(e) metal borides.

20. Which of the following oxides of nitrogen contains N—O—N bond?
(a) Dinitrogen oxide
(b) Nitrogen monoxide
(c) Dinitrogen pentoxide
(d) Dinitrogen trioxide
(e) Dinitrogen tetroxide

21. Which of the following transition metals of 3*d* series has the lowest melting point?
(a) Ti (Z = 22) (b) V (Z = 23)
(c) Cr (Z = 24) (d) Mn (Z = 25)
(e) Fe (Z = 26)

22. Which of the following ions has the same number of unpaired electrons as present in V^{3+} ?
(a) Ti^{3+} (b) Fe^{3+}
(c) Ni^{2+} (d) Cr^{3+}
(e) Mn^{2+}

23. Among the following actinide pairs, the maximum oxidation states is shown by
(a) U and Np (b) Np and Pu
(c) Pu and Am (d) U and Pa
(e) Th and Pu

24. Among the transition metals of 3*d* series, the one that has the highest negative M^{2+}/M standard electrode potential is
(a) Ti (b) Cu
(c) Mn (d) Ni
(e) Zn

25. The enthalpies of solution for copper sulphate pentahydrate and anhydrous copper sulphate are respectively –11.7 and –65.5 kJ mol^{-1}. The hydration enthalpy of anhydrous copper sulphate is
(a) 53.8 kJ mol^{-1} (b) –9.8 kJ mol^{-1}
(c) –77.2 kJ mol^{-1} (d) –53.8 kJ mol^{-1}
(e) 77.2 kJ mol^{-1}

26. The standard enthalpy of formation of $NH_{3(g)}$ is –91.8 kJ mol^{-1}. The amount of heat required to decompose 34 g of $NH_{3(g)}$ into its elements is

(a) 183.6 kJ (b) 91.8 kJ
(c) 45.9 kJ (d) 137.7 kJ
(e) 275.4 kJ

27. Calculate the work done by 16 g of oxygen gas (assume ideal behaviour) of molar mass 32 g mol^{-1} undergoing isothermal reversible expansion at 300 K from an initial volume of 2.5 L to the final volume of 25 L in litre atm.

($R = 8.2 \times 10^{-2}$ L atm K^{-1} mol^{-1})

(a) –56.64 (b) 28.32
(c) 113.28 (d) 56.64
(e) –113.28

28. In which one of the following the increase of pressure favours the backward reaction?

(a) Formation equilibrium of ammonia from $N_{2(g)}$ and $H_{2(g)}$
(b) Decomposition equilibrium of $HI_{(g)}$ to $H_{2(g)}$ and $I_{2(g)}$
(c) Synthesis of $SO_{3(g)}$ by contact process
(d) Production of 'syngas' by coal gasification
(e) Formation equilibrium of Fe_3O_4 by action of steam on iron

29. At 800 K in a sealed vessel, for the equilibrium $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, the equilibrium concentrations of $N_{2(g)}$, $O_{2(g)}$ and $NO_{(g)}$ are respectively 0.36×10^{-3} M, 4.41×10^{-3} M and 1.4×10^{-3} M. Then, the value of K_c for the reaction $NO_{(g)} \rightleftharpoons 1/2N_{2(g)} + 1/2O_{2(g)}$ at 800 K is

(a) 1.1 (b) 0.9
(c) 3×10^3 (d) 9×10^{-3}
(e) 0.33

30. The solubility product of a salt MX_2 in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is

(a) 1×10^{-4} M (b) 4×10^{-4} M
(c) 16×10^{-6} M (d) 2×10^{-4} M
(e) 12×10^{-2} M

31. Which one of the following species cannot act as both Bronsted acid and base?

(a) H_2O (b) HCO_3^-
(c) HSO_4^- (d) NH_2^-
(e) NH_3

32. The correct equation for the degree of association 'α' of an associating solute, '*n*' molecules of which undergoes association in solution, is

(a) $\alpha = \frac{n(i-1)}{1-n}$ (b) $\alpha = \frac{i(n-1)}{1+n}$
(c) $\alpha = \frac{i(n+1)}{1-n}$ (d) $\alpha = \frac{i(n+1)}{n-1}$
(e) $\alpha = \frac{n(1-i)}{1-n}$

33. The vapour pressure of a solvent at 293 K is 100 mm Hg. Then the vapour pressure of a solution containing 1 mole of a strong electrolyte (AB_2) in 99 moles of the solvent at 293 K is (assume complete dissociation of solute)

(a) 103 mm Hg (b) 99 mm Hg
(c) 97 mm Hg (d) 101 mm Hg
(e) 98 mm Hg

34. The correct order of osmotic pressure of 0.01 M aqueous solution of the following is

(a) Sucrose > CH_3COOH > KCl
(b) CH_3COOH > Sucrose > KCl
(c) Sucrose > KCl > CH_3COOH
(d) KCl > Sucrose > CH_3COOH
(e) KCl > CH_3COOH > Sucrose

35. Among the following elements, which one exhibits both positive and negative oxidation states?

(a) Cs (b) Ne
(c) I (d) F
(e) K

36. Choose the disproportionation reaction among the following redox reactions.

(a) $3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$
(b) $P_{4(s)} + 3NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow PH_{3(g)} + 3NaH_2PO_{2(aq)}$
(c) $Cl_{2(g)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(s)}$
(d) $Cr_2O_{3(s)} + 2Al_{(s)} \rightarrow Al_2O_{3(s)} + 2Cr_{(s)}$
(e) $2NaH_{(s)} \rightarrow 2Na_{(s)} + H_{2(g)}$

37. Standard electrode potentials of three metals *X*, *Y* and *Z* are 0.52 V, –2.87 V and –0.44 V respectively. The reducing power of these metals are

(a) $X > Y > Z$ (b) $X > Z > Y$
(c) $Y > X > Z$ (d) $Z > X > Y$
(e) $Y > Z > X$

38. In a first order reaction 80% of the reactant at an instant was reduced to 8% in 4606 seconds. The rate constant of the reaction is
(a) $2.303 \times 10^{-4}\ s^{-1}$ (b) $4.606 \times 10^{-3} s^{-1}$
(c) $5.000 \times 10^{-3}\ s^{-1}$ (d) $5.000 \times 10^{-4} s^{-1}$
(e) $4.606 \times 10^{-4}\ s^{-1}$

39. The decomposition of N_2O_5 in CCl_4 at 318 K is studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.4 mol L^{-1} and after 200 minutes, it is reduced to 2.00 mol L^{-1}. What is the rate of production of NO_2 during this period in mol L^{-1} min^{-1} ?
(a) 4×10^{-3} (b) 2×10^{-3}
(c) 1×10^{-3} (d) 2×10^{-4}
(e) 5×10^{-3}

40. In a first order reaction, the concentration of the reactant decreases from 0.6 M to 0.3 M in 30 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is
(a) 60 min (b) 30 min
(c) 15 min (d) 50 min
(e) 90 min

41. The correct ascending order of adsorption of the following gases on the same mass of charcoal at the same temperature and pressure is
(a) $CH_4 < H_2 < SO_2$ (b) $H_2 < CH_4 < SO_2$
(c) $SO_2 < CH_4 < H_2$ (d) $H_2 < SO_2 < CH_4$
(e) $CH_4 < SO_2 < H_2$

42. When H_2 and CO are reacted in the presence of Cu catalyst, the product/s obtained is/are
(a) methanol (b) methanal
(c) methane and H_2O (d) acetic acid
(e) ethanol.

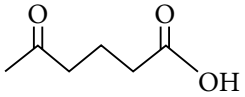
43. Which of the following statements is incorrect about physisorption?
(a) It is reversible in nature.
(b) It forms multilayer.
(c) It involves high activation energy.
(d) The extent of physisorption decreases with increase of temperature.
(e) It increases with increase in surface area.

44. The compound $[Pt(NH_3)_2Cl_2]$ can exhibit
(a) linkage isomerism
(b) coordination isomerism
(c) optical isomerism
(d) geometrical isomerism
(e) ionization isomerism.

45. Which one among the following is a homoleptic complex?
(a) Tris(ethane-1,2-diamine)cobalt(III) chloride
(b) Triamminetriaquachromium(III) chloride
(c) Diamminechloridonitrito-*N*-platinum(II)
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(e) Pentamminecarbonatocobalt(III) chloride

46. The coordination number, oxidation number and the number of *d*-electrons in the metal ion of the complex $[CoCl_2(en)_2]Cl$, are respectively (atomic number of Co = 27)
(a) 4, 3 and 6 (b) 6, 2 and 6
(c) 6, 6 and 3 (d) 4, 2 and 6
(e) 6, 3 and 6

47. What is the IUPAC name of the following compound?



(a) Hexa-2,6-dienone-6-ol
(b) 2-Ketohexanoic acid
(c) 5-Ketohexanoic acid
(d) 2-Oxohexanoic acid
(e) 5-Oxohexanoic acid

48. The numbers of σ and π-bonds present in 1, 3-butadiene are respectively
(a) 9 and 2 (b) 8 and 2
(c) 9 and 3 (d) 9 and 1
(e) 8 and 1

49. Which one of the following is an aromatic compound?
(a) Cyclopentadienyl cation
(b) Cycloheptatrienyl cation
(c) Cycloheptatrienyl anion
(d) Cycloheptatriene
(e) Cyclopentadiene

50. *n*-Hexane on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium supported over alumina, yields
(a) 1-hexene (b) 2-hexene
(c) benzene (d) 2-methylpentane
(e) 2,2-dimethylbutane.

51. Which one of the following is not an isomer of 3-methylbut-1-yne?
(a) Pent-1-yne (b) Buta-1,3-diene
(c) Pent-2-yne (d) Penta-1,3-diene
(e) 2-Methylbuta-1,3-diene

52. The correct decreasing order of acidic character of hydrogen in ethane, ethene and ethyne is
(a) ethane > ethene > ethyne
(b) ethene > ethane > ethyne
(c) ethyne > ethane > ethene
(d) ethyne > ethene > ethane
(e) ethane > ethyne > ethene.

53. On ozonolysis, one molecule of a hydrocarbon produces two moelcules of ethanal and one molecule of ethanedial. The hydrocarbon could be
(a) 1, 3-hexadiene
(b) 1, 4-cyclohexadiene
(c) 1, 4-hexadiene
(d) 2, 4-hexadiene
(e) 1, 3-cyclohexadiene.

54. Acid catalysed hydration of alkene is an example for
(a) free radical substitution
(b) nucleophilic substitution
(c) nucleophilic addition
(d) electrophilic addition
(e) electrophilic substitution.

55. Which one of the following undergoes nitration reaction most readily?
(a) Acetophenone (b) Benzonitrile
(c) Benzaldehyde (d) Benzoic acid
(e) Benzene

56. The total number of optical isomers possible for 2, 3-dibromobutane is
(a) 2 (b) 4
(c) 0 (d) 3
(e) 8

57. Dehydration of which one of the following alcohols produces an alkene exhibiting *cis-trans* isomerism?
(a) Isopropyl alcohol (b) Tertiary butyl alcohol
(c) *n*-Butyl alcohol (d) Neopentyl alcohol
(e) 3-Pentanol

58. The products expected to be formed in the Wurtz reaction of a mixture of neopentyl bromide and isobutyl bromide are
(i) 2,2,4-trimethylpentane
(ii) 2,2,5,5-tetramethylhexane
(iii) 2,2,4,4-tetramethylhexane
(iv) 2,5-dimethylhexane
(v) 2,2,5-trimethylhexane
(a) (ii), (iii) and (v) (b) (ii), (iv) and (v)
(c) (i), (iv) and (v) (d) (i), (iii) and (v)
(e) (i), (ii) and (iv)

59. Which one of the following organohalogen compounds when heated with alcoholic potassium hydroxide does not undergo dehydrohalogenation reaction?
(a) Secondary butyl chloride
(b) Isopropyl chloride
(c) Neopentyl chloride
(d) Isobutyl chloride
(e) Tertiary butyl chloride

60. By which one of the following reactions ketones cannot be prepared?
(a) Hydration of alkynes
(b) Hydrolysis of gem-dihalides
(c) Dry distillation of calcium carboxylates
(d) Stephen's reaction
(e) Ozonolysis of appropriately substituted alkenes

61. When a mixture of benzaldehyde and acetophenone is treated with dilute NaOH at 293 K, it forms
(a) 2, 3-diphenylpropanal
(b) 1, 1-diphenylpropan-2-one-1-ol
(c) 1,3-diphenylprop-2-en-1-one
(d) 1,2-diphenylprop-2-en-1-one
(e) 1,3-diphenylprop-2-en-1-al.

62. Glutaric acid is
(a) butane-1,4-dioic acid
(b) propane-1,3-dioic acid
(c) pentane-1,5-dioic acid
(d) hexane-1,6-dioic acid
(e) ethanedioic acid.

63. 4-Methoxyacetophenone can be prepared from anisole by
(a) Reimer–Tiemann reaction
(b) Kolbe's reaction
(c) Friedel–Craf s reaction
(d) Wurtz reaction
(e) Cannizzaro reaction.

64. The total number of structural isomers possible for an amine with molecular formula $C_4H_{11}N$ is
(a) 6 (b) 5
(c) 7 (d) 4
(e) 8

65. Which one of the following amines cannot be prepared by Gabriel phthalimide synthesis?
(a) Ethylamine (b) Isopropylamine
(c) *n*-Propylamine (d) Ethylmethylamine
(e) Allylamine

66. Which one of the following amines forms a non-acidic and alkali insoluble product with *p*-toluenesulphonyl chloride?
(a) Tertiary butylamine
(b) *n*-Butylamine
(c) Isobutylamine
(d) Diethylamine
(e) *N*, *N*-Dimethylethylamine

67. Which of the following compounds is most basic?
(a) Aniline (b) Cyclohexylamine
(c) *o*-Nitroaniline (d) *o*-Toluidine
(e) *p*-Methoxyaniline

68. Glucose does not react with
(a) hydroxylamine (b) conc. HNO_3
(c) acetic anhydride (d) sodium bisulphite
(e) Br_2/H_2O.

69. Which of the following is a water soluble vitamin?
(a) Vitamin A (b) Vitamin D
(c) Vitamin B_1 (d) Vitamin E
(e) Vitamin K

70. The polymer used in the manufacture of squeeze bottles is
(a) polystyrene (b) teflon
(c) polypropene (d) high density polythene
(e) low density polythene.

71. The drug Tegamet is
(a) analgesic (b) antidepressant
(c) anaesthetic (d) antacid
(e) antibiotic.

72. Which one of the following is a cationic detergent?
(a) Sodium laurylsulphate
(b) Cetyltrimethyl ammonium bromide
(c) Sodium dodecylbenzene sulphonate
(d) Glyceryl palmitate
(e) Glyceryl oleate.

SOLUTIONS

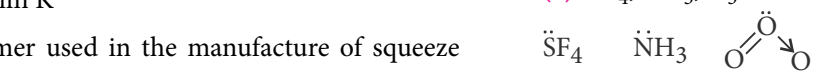
1. **(c):** (a) For a particular value of n, $l = 0$ to $n - 1$.
$\therefore$ For $n = 3$, l cannot be equal to 3.
(b) For a particular value of l, $m_l = -l$ to l including zero.
$\therefore$ For $l = 1$, m_l cannot be 2 which is greater than l.
(d) $m_s = +\frac{1}{2}, -\frac{1}{2}$ $\therefore$ m_s cannot be equal to zero.
(e) m_l cannot be greater than l.

2. **(a):** $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$
According to equation, 1 mole of $CaCO_3$ reacts completely with 2 moles of HCl.
Number of moles of HCl $= \frac{20}{1000} \times 1 \text{ mol} = 0.02 \text{ mol}$
$\therefore$ Number of moles of $CaCO_3 = 0.01$ mol
Hence, mass of $CaCO_3$ required to react completely with HCl $= (0.01 \times 100) = 1$ g

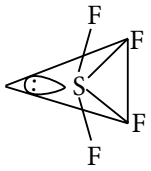
3. **(e):** (a) 16 g of $O_2 = \frac{16}{32} = 0.5$ mol
(b) 16 g of $NO_2 = \frac{16}{46} = 0.35$ mol
(c) 4 g of $N_2 = \frac{4}{28} = 0.14$ mol
(d) 2 g of $H_2 = \frac{2}{2} = 1$ mol
(e) 32 g of $N_2 = \frac{32}{28} = 1.14$ mol

4. **(a):** 2 M *i.e.*, 2 moles in 1000 mL
Wt. of 1000 mL solution = 1200 g
Wt. of solvent = 1200 – 200 = 1000 g
$\therefore$ Molality = 2 m

5. **(b):** SF_4, NH_3, O_3



6. **(b):** SF_4 is see saw shaped.



7. **(c):**

Species	Bond order	Magnetic behaviour
F_2	1	Diamagnetic
O_2	2	Paramagnetic
N_2	3	Diamagnetic
O_2^{2-}	1	Diamagnetic
Li_2	1	Diamagnetic
B_2	1	Paramagnetic

Helium and neon are monatomic and diamagnetic.

8. (c): Cl—S̈—Cl

XeF_4 and $XeOF_2$ have expanded octets while $AlCl_3$ and BF_3 have incomplete octets.

9. (e): For a mixture of non-reacting gases, partial pressure ∝ number of moles.
For equal masses,

$$n_{He} : n_{O_2} : n_{SO_2} = \frac{1}{4} : \frac{1}{32} : \frac{1}{64}$$

$$\therefore \quad p_{He} : p_{O_2} : p_{SO_2} = 16 : 2 : 1$$

10. (c): Easily liquif able gases have higher critical temperature.

11. (d): NaCl – Diamagnetic
MnO – Antiferromagnetic
$CrCl_3$ – Paramagnetic
CrO_2 – Ferromagnetic
$MgFe_2O_4$ – Ferrimagnetic

12. (e)

13. (a): A cation is always smaller than its atom and also on moving from lef to right in a period atomic and ionic size decrease.
$\therefore$ Mg > Al and $Mg^{2+} > Al^{3+}$

14. (b)

15. (a): Be forms covalent compounds due to its smaller size and high ionization enthalpy.

16. (a)

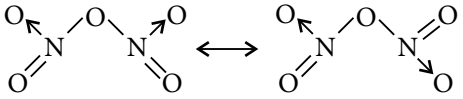
17. (c): $Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_4\downarrow} + 2NaCl$
(Gives yellow colour in flame test)

18. (a): The P—H bond present in H_3PO_2 imparts reducing property to the acid.

$$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag\downarrow + 4HNO_3 + H_3PO_4$$

19. (e)

20. (c): Dinitrogen pentoxide



21. (d): In f rst transition series Mn has abnormally low melting point. This can be explained on the basis that Mn has exactly half-f lled *d*-orbitals. As a result the electronic conf guration is stable, electrons are held tightly by the nucleus, delocalisation is less and metallic bond is much weaker.

22. (c):

Species	Outer electronic configuration	No. of unpaired electrons
Ti^{3+}	$3d^1$	1
Fe^{3+}	$3d^5$	5
Ni^{2+}	$3d^8$	2
Cr^{3+}	$3d^3$	3
Mn^{2+}	$3d^5$	5
V^{3+}	$3d^2$	2

23. (b): They both show highest oxidation state of +7.

24. (a): The M^{2+}/M standard electrode potential value of Ti is –1.63 V.

25. (d): Given :

(i) $CuSO_{4(s)} + aq \longrightarrow CuSO_{4(aq)}$; $\Delta_{sol}H = -65.5$ kJ mol^{-1}

(ii) $CuSO_4.5H_2O_{(s)} + aq \longrightarrow CuSO_{4(aq)}$; $\Delta_{sol}H = -11.7$ kJ mol^{-1}

To f nd : $CuSO_{4(s)} + 5H_2O_{(l)} \longrightarrow CuSO_4.5H_2O_{(s)}$; $\Delta_{hyd}H = ?$

Equation (i) can be written in two steps as :

(iii) $CuSO_{4(s)} + 5H_2O_{(l)} \longrightarrow CuSO_4.5H_2O_{(s)}$; $\Delta H = \Delta H_1$ kJ mol^{-1}

(iv) $CuSO_4.5H_2O_{(s)} + aq \longrightarrow CuSO_{4(aq)}$; $\Delta H = \Delta H_2$ kJ mol^{-1}

According to Hess's law,

$\Delta H_1 + \Delta H_2 = -65.5$ kJ mol^{-1}

Further, equations (ii) and (iv) are same.

$\therefore \quad \Delta H_2 = -11.7$ kJ mol^{-1}

Putting this value above, we get

$\Delta H_1 - 11.7 = -65.5$

or $\Delta H_1 = -65.5 + 11.7$ kJ $= -53.8$ kJ mol^{-1}

26. (a): The standard enthalpy of formation of $NH_{3(g)}$ is –91.8 kJ mol^{-1}.

$\Rightarrow$ 91.8 kJ of heat energy is required to decompose 1 mole of NH_3.

Hence, for 34 g of NH_3 (2 moles) amount of heat required = 2 × 91.8 kJ = 183.6 kJ

27. (b): For isothermal reversible expansion of an ideal gas

$$w = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{16}{32} \times 8.2 \times 10^{-2} \times 300 \times \log \frac{25}{2.5}$$

$= -28.32$ L atm.

Hence work done by the system = 28.32 L atm.

28. (d): (a) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$n_p < n_r$, hence increase of pressure will favour forward reaction.

(b) $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

$n_p = n_r$, hence pressure has no ef ect.

(c) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$n_p < n_r$, hence increase of pressure will favour forward reaction.

(d) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

$n_p > n_r$, hence increase of pressure will favour backward reaction.

(e) $3Fe_{(s)} + \underset{\text{(Steam)}}{4H_2O_{(g)}} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

$n_p = n_r$, hence pressure has no ef ect.

29. (b): $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_c = \frac{(1.4\times10^{-3})^2}{0.36\times10^{-3}\times4.41\times10^{-3}} = 1.23$$

$$NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$$

$$\frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{1.23}} = 0.9$$

30. (a): $\underset{s}{MX_2} \rightleftharpoons \underset{s}{M^{2+}} + \underset{2s}{2X^-}$

$K_{sp} = s.(2s)^2 = 4s^3$

$$\Rightarrow \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4\times10^{-12}}{4}} = 1\times10^{-4}\ \text{M}$$

31. (d)

32. (a): If n simple molecules of the solute A associate to form the associated molecule A_n so that we have the equilibrium :

$$nA \rightleftharpoons A_n$$

If α is the degree of association and we start with one mole of A, then at equilibrium

Number of moles of $A = 1 - \alpha$

Number of moles of $A_n = \alpha/n$

$\therefore$ Total number of moles $= 1 - \alpha + \alpha/n$

Since the colligative property is proportional to the number of moles of the solute present in solution,

therefore, van't Hof factor $i = \dfrac{1-\alpha+\frac{\alpha}{n}}{1}$

hence, $\alpha = \dfrac{n(i-1)}{1-n}$

33. (c): $\dfrac{p^\circ - p_s}{p^\circ} = i \times \dfrac{n_2}{n_1+n_2}$

$$\frac{100-p_s}{100} = 3\times\frac{1}{100}$$

$p_s = 97$ mm Hg

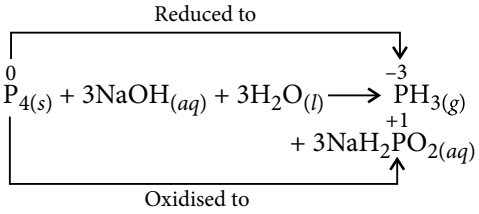
34. (e): $\pi = iCRT$

$\Rightarrow \quad \pi \propto i$

Hence, $\underset{\text{(Strong electrolyte)}}{KCl} > \underset{\text{(Weak acid)}}{CH_3COOH} > \underset{\text{(Non electrolyte)}}{\text{Sucrose}}$

35. (c)

36. (b): In disproportionation reaction, the same element undergoes reduction as well as oxidation.



37. (e): Lower the reduction potential, higher will be the reducing power.

38. (d): $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t} = \dfrac{2.303}{4606}\log\dfrac{80}{8} = 5\times10^{-4}\ s^{-1}$

39. (a): $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$\dfrac{1}{2}\times$ Rate of disappearance of N_2O_5

$= \dfrac{1}{4}\times$ Rate of production of NO_2

Rate of production of NO_2

$= \dfrac{4}{2}\times$ Rate of disappearance of N_2O_5

$$= 2\left(\frac{2.4-2.0}{200}\right) = \frac{0.4}{100} = 4\times10^{-3}\ \text{mol}\ L^{-1}\ \text{min}^{-1}$$

40. (a): $0.1 \xrightarrow{t_{1/2}} 0.05 \xrightarrow{t_{1/2}} 0.025$

Hence, time taken $= 2 \times t_{1/2} = 2 \times 30 = 60$ min

41. (b): Higher the critical temperature of a gas, greater is the amount of gas adsorbed.

Critical temperature (in kelvin) of

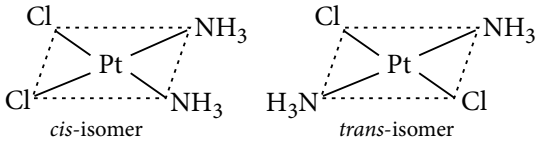
$$\underset{33.2}{H_2} < \underset{190.6}{CH_4} < \underset{430.3}{SO_2}$$

Hence, the order the of adsorption will be $H_2 < CH_4 < SO_2$.

42. (b): $CO_{(g)} + H_{2(g)} \xrightarrow{Cu} HCHO_{(g)}$

43. (c): Physisorption does not require any activation energy.

44. (d): $[Pt(NH_3)_2Cl_2]$ exhibits geometrical isomerism.



45. (a): Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes.

46. (e): Ethylenediamine (*en*) is a didentate ligand hence,

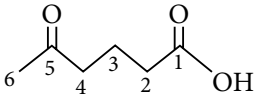
Coordination number of Co = 6

Oxidation number :

$x - 2 = +1 \quad \Rightarrow \quad x = +3$

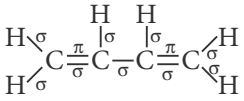
Outer electronic conf guration of Co^{3+} is $3d^6$.

47. (e):



5-Oxohexanoic acid

48. (a):



49. (b):

Cyclopentadienyl cation
Planar, 4π-electrons
(Antiaromatic)

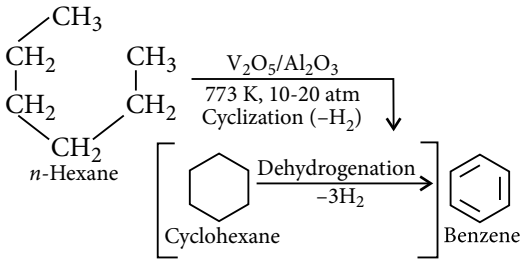
Cycloheptatrienyl cation
Planar, 6π-electrons spread over the entire ring,
(Aromatic)

Cycloheptatrienyl anion
Planar, 8π-electrons
(Antiaromatic)

Cycloheptatriene
Non planar, 6π-electrons
(Non aromatic)

Cyclopentadiene
Non planar, 4π-electrons
(Non aromatic)

50. (c):



51. (b): Isomers have same molecular formula but dif erent structures.

52. (d): $\overset{sp}{HC}\equiv\overset{sp}{CH} > \overset{sp^2}{H_2C}=\overset{sp^2}{CH_2} > \overset{sp^3}{H_3C}-\overset{sp^3}{CH_3}$

More the *s*-character of the hybrid orbitals, more electronegative is the atom and more is the acidic character of hydrogen attached to that carbon.

53. (d): $CH_3CH=CH-CH=CHCH_3 \xrightarrow{\text{Ozonolysis}} \underset{\text{Ethanal}}{2CH_3CHO} + \underset{\text{Ethanedial}}{OHC-CHO}$

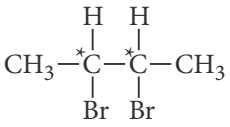
2, 4-Hexadiene

54. (d)

55. (e): Nitration reaction is an electrophilic substitution reaction. Hence benzene will undergo nitration most easily because all other compounds contain deactivating groups.

56. (d): When the molecule can be divided into equal halves, *i.e.*, the molecule has symmetry and the number (n) of asymmetric carbon atoms is even, then the total number of optical isomers

$= 2^{(n-1)} + 2^{(n/2)-1}$



The molecule has symmetry *i.e.*, can be divided into equal halves and it has two chiral carbon atoms ($n = 2$).

$\therefore$ No. of optical isomers $= 2^{(2-1)} + 2^{(2/2)-1} = 3$

57. (e): (a) $\underset{\text{Isopropyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-OH} \xrightarrow[H^+]{\text{Dehydration}} CH_3-CH=CH_2$

(b) $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow[H^+]{\text{Dehydration}} CH_3-\overset{CH_2}{\overset{||}{C}}-CH_3$

Tertiary butyl alcohol

(c) $\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H^+]{\text{Dehydration}} CH_3-CH_2-CH=CH_2$

(d) $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-OH \xrightarrow[H^+]{\text{Dehydration}} \underset{\text{(Major)}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CHCH_3} + \underset{\text{(Minor)}}{CH_3-\overset{CH_2}{\overset{||}{C}}-CH_2CH_3}$

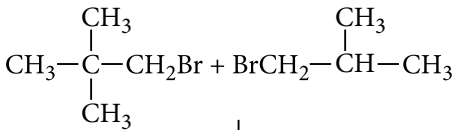
Neopentyl alcohol

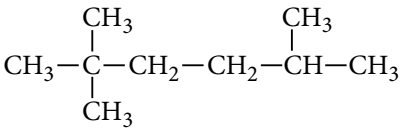
(e) $CH_3-CH_2-\underset{\underset{\text{3-Pentanol}}{}}{\overset{\overset{OH}{|}}{CH}}-CH_2-CH_3 \xrightarrow[H^+]{\text{Dehydration}} CH_3-CH=CH-CH_2-CH_3$

Pent-2-ene

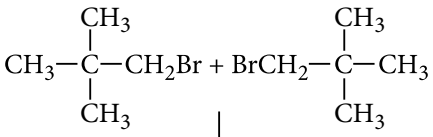
Only pent-2-ene has two dif erent groups attached to doubly bonded carbon atoms hence, it will show *cis-trans* isomerism.

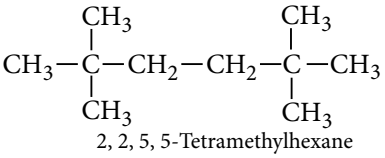
58. (b): Wurtz reaction can occur in the following ways :



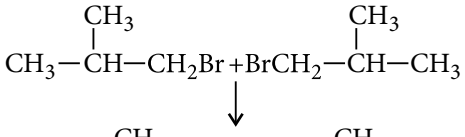


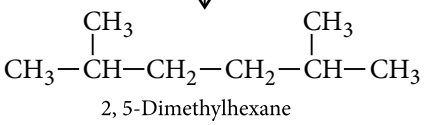
2, 2, 5-Trimethylhexane





2, 2, 5, 5-Tetramethylhexane





2, 5-Dimethylhexane

59. (c): Neopentyl chloride does not have any β-hydrogen, hence it does not undergo dehydrohalogenation reaction.

60. (d): Stephen's reaction is used for the preparation of aldehydes.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

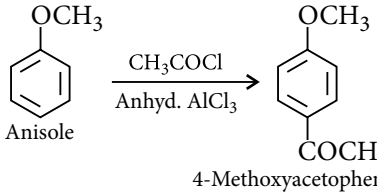
61. (c): It is a cross aldol reaction.

$C_6H_5CH{=}O + CH_3-CO-C_6H_5 \xrightarrow[-H_2O]{NaOH} C_6H_5CH{=}CH-CO-C_6H_5$

1,3-Diphenylprop-2-en-1-one

62. (c)

63. (c): It is a Friedel – Craf s reaction.

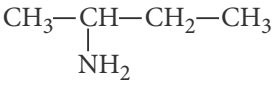


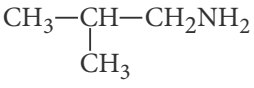
Anisole

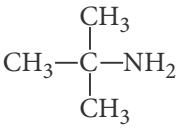
4-Methoxyacetophenone

64. (e): The isomers are

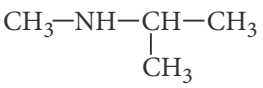
$CH_3-CH_2-CH_2-CH_2-NH_2$



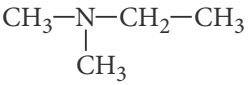




$CH_3-NH-CH_2-CH_2-CH_3$



$CH_3-CH_2-NH-CH_2-CH_3$



65. (d): Gabriel phthalimide synthesis is used for the preparation of 1° aliphatic amines. Ethylmethylamine is a 2° amine.

66. (d): Secondary amines give an alkali insoluble product with *p*-toluenesulphonyl chloride.

67. (b): In cyclohexylamine, there is no delocalisation of the lone pair of electrons on nitrogen whereas in aniline, *o*-nitroaniline, *o*-toluidine and *p*-methoxyaniline, the lone pair of electrons is delocalised on benzene ring.

68. (d) **69. (c)** **70. (e)**

71. (d) **72. (b)**

CHALLENGING PROBLEMS

1. Boat form of cyclohexane has
   (a) relative energy about 28.9 kJ mol^{-1} higher than that of chair form
   (b) relative energy about 28.9 kJ mol^{-1} lower than that of chair form
   (c) relative energy about 44 kJ mol^{-1} higher than that of chair form
   (d) relative energy about 22.2 kJ mol^{-1} lower than that of chair form.

2. From B_2H_6 all of them can be prepared except
   (a) H_3BO_3 (b) $NaBH_4$
   (c) $B_2(CH_3)_6$ (d) B_2O_3

3. Which pair shows a contraction in volume on mixing along with evolution of heat?
   (a) $CHCl_3 + C_6H_6$ (b) $H_2O + HCl$
   (c) $H_2O + HNO_3$ (d) All of these

4. Among the following, the most reactive towards alcoholic KOH is
   (a) $CH_2=CHBr$ (b) $CH_3COCH_2CH_2Br$
   (c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$

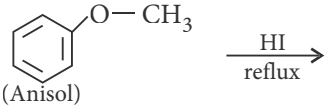
5. One mole of peroxydisulphuric acid on hydrolysis produces
   (a) 1 mole of H_2O_2 and 1 mole of H_2SO_4
   (b) 1 mole of H_2O_2 and 2 moles of H_2SO_4
   (c) 1 mole of H_2SO_5 and 1 mole of H_2SO_4
   (d) depends upon conditions of hydrolysis whether (*b*) or (*c*).

6. H_3PO_4 is a tribasic acid and one of its salts is NaH_2PO_4. What volume of 1 M NaOH should be added to 12 g NaH_2PO_4 (mol. mass = 120) to exactly convert it into Na_3PO_4?
   (a) 100 mL (b) 300 mL
   (c) 200 mL (d) 80 mL

7. The major product of the reaction of hypochlorous acid with ethyne in diffused sunlight is
   (a) $Cl-C\equiv C-Cl$ (b) $CH_2Cl-CHO$
   (c) $Cl_2CH-CHO$ (d) $Cl_2CH-COOH$

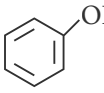
8. Which products are expected from the disproportionation reaction of hypochlorous acid?
   (a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$
   (c) HCl and Cl_2O (d) HCl and $HClO_3$

9. In a face-centred cubic arrangement of *A* and *B* atoms in which *A* atoms are at the corners of the unit cell and *B* atoms are at the face centres, one of the *A* atoms is missing from one corner in unit cell. The simplest formula of the compound is
   (a) A_7B_3 (b) AB_3
   (c) A_7B_{24} (d) $A_{8/7}B_3$

10. 

(Anisol)

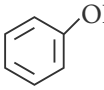
Mechanism followed and the major products are

(a) S_N1; 

, CH_3I

(b) S_N2; 

, CH_3OH

(c) S_N2; 

, CH_3I

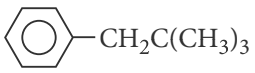
(d) S_N1; 

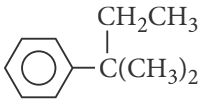
, CH_3OH

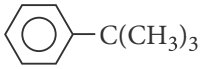
11. Which of the following is incorrect about borax?
   (a) Produces alkaline solution in water.
   (b) Produces buffer solution in water.
   (c) Produces blue bead on heating with $CaSO_4$.
   (d) Used as an acidic flux.

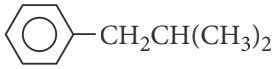
12. The compressibility factor (*Z*) for one mole of a gas is more than unity at STP. Therefore
   (a) $V = 11.2$ L (b) $V < 22.38$ L
   (c) $V > 22.38$ L (d) $V = 22.38$ L

13. Neopentyl chloride reacts with benzene in presence of a Lewis acid ($AlCl_3$) to form

(a) 

(b) 

(c) 

(d) 

14. Select the incorrect statement about alkaline earth metals.
(a) Solubility of sulphates decreases down the group.
(b) Solubility of hydroxides decreases down the group.
(c) Thermal stability of carbonates increases down the group.
(d) Basic nature increases down the group.

15. An endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
(a) ΔH = –ve, ΔS = +ve
(b) both ΔH and ΔS are +ve
(c) both ΔH and ΔS are –ve
(d) ΔH = +ve, ΔS = –ve

16.  does not show the characteristic properties of >C = O group, because of
(a) resonance
(b) +*I* effect of *R* group
(c) weak bond between 'O' and 'H'
(d) —OH group which is electron withdrawing group.

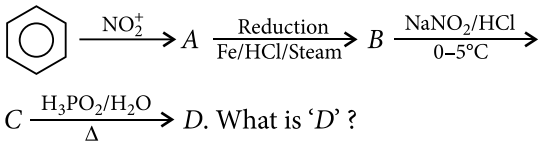
17. Graphite $\xrightarrow[\text{(oxidation)}]{\text{Strong oxidising agent}} \underset{\text{(acid)}}{X} \xrightarrow[\text{Dehydration}]{\Delta} Y$. *Y* is
(a) C_3O_2 (b) CO
(c) CO_2 (d) $C_{12}O_9$

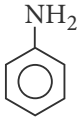
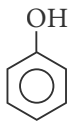
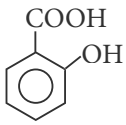
18. If the rate of reaction is $r = k[X]^{1/3}[Y]^{2/3}$, what is the unit of rate constant?
(a) $mol^{1/3}\ L^{-2/3}\ time^{-1}$
(b) $mol^{2/3}\ L^{1/3}\ time^{-1}$
(c) $mol^{1/6}L^{-1/6}\ time^{-1}$
(d) $mol^{0}L^{0}\ time^{-1}$

19. Which of the following cannot be used to distinguish between HCOOH and CH_3COOH?
(a) Tollens' reagent (b) $FeCl_3$ (dilute)
(c) $NaHCO_3$ (*aq.*) (d) $SOCl_2$

20. Which of the following contains two S-atoms bonded to each other?
(a) $H_2S_2O_2$ (b) $H_2S_2O_4$
(c) $H_2S_2O_6$ (d) All of these

21. Which of the following statements is incorrect?
(a) Adsorption lowers the activation energy of reaction.
(b) In a micelle, polar end is at the inner surface.
(c) Cetyltrimethylammonium bromide forms cationic micelle.
(d) When pressure has no effect on extent of adsorption, the pressure is known as saturation pressure.

22. 
What is '*D*' ?

(a) 
(b) 
(c) 
(d) 

23. Which of the following is incorrect *w.r.t.* noble gases?
(a) Kr is produced during radioactive disintegration.
(b) Rn is radioactive.
(c) O_2 + He is used by divers.
(d) Ne light cannot be stopped by fog.

24. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solution should the other electrode be immersed to get maximum EMF?
(a) 0.1 M HCl (b) 0.1 M CH_3COOH
(c) 0.1 M H_3PO_4 (d) 0.1 M H_2SO_4

25. In Liebermann's nitroso test
(a) phenol reacts with nitroso acid
(b) aniline reacts with nitrous acid
(c) phenol and aniline react with $NaNO_2$ + HCl
(d) none of the above.

26. Which of the following pairs of ions do not form alums?
(a) NH_4^+, K^+ (b) Li^+, Mg^{2+}
(c) Fe^{3+}, Al^{3+} (d) Fe^{3+}, Cr^{3+}

27. In the titration of Na_2CO_3 with HCl, indicator used is
(a) phenolphthalein
(b) methyl orange
(c) both (a) and (b)
(d) none of these.

28. The number of chiral C-atoms in glucose and fructose are respectively
(a) 3, 3 (b) 4, 4
(c) 3, 4 (d) 4, 3

29. Which of the following does not produce any gaseous product when reacts with water?
(a) Ca_3N_2 (b) CaC_2
(c) CaO (d) Ca_3P_2

30. The stabilisation of a dispersed phase in a lyophobic colloid is due to
(a) the adsorption of charged substances on dispersed phase
(b) the viscosity of the medium
(c) the formation of an electrical layer between two phases
(d) none of these.

31. In soaps, sodium rosinate works
(a) to enhance lathering properly
(b) as antiseptic
(c) as hardening agent
(d) all of these.

32. In which of the following compounds, Ce is in its most stable oxidation state?
(a) CeH_2
(b) $Ce(OH)_3$
(c) $(NH_4)_2[Ce(NO_3)_6]$
(d) $Ce(SO_4)_2$

33. Let the solubilities of AgCl in H_2O, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.05 M $AgNO_3$ be s_1, s_2, s_3, s_4 respectively. What is the correct relationship between these quantities?
(K_{sp} for AgCl = 1.5×10^{-10})
(a) $s_1 > s_2 > s_3 > s_4$ (b) $s_1 > s_2 = s_3 > s_4$
(c) $s_1 > s_3 > s_2 > s_4$ (d) $s_4 > s_2 > s_3 > s_1$

34. Orlon is a polymer of
(a) $CH_2{=}CH{-}C_6H_5$
(b) $CH_2{=}CH{-}CN$
(c) $CF_2{=}CF_2$
(d) $CH_3{-}CH{=}CH_2$

35. Which method is not correct for ref ning of crude metals?
(a) Distillation : Zinc and mercury
(b) Liquation : Tin
(c) van Arkel : Zirconium
(d) Mond process : Lead

36. The energy required to break one mole of Cl—Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single Cl—Cl bond is ($c = 3 \times 10^8$ m s^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 493 nm (b) 594 nm
(c) 640 nm (d) 700 nm

37. Which amino acid can form covalent sulphur—sulphur bonds?
(a) Cysteine (b) Glycine
(c) Proline (d) Methionine

38. In $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ species, the hybridisation states at the Ni-atom respectively are
(a) sp^3, dsp^2, dsp^2 (b) sp^3, dsp^2, sp^3
(c) sp^3, sp^3, dsp^2 (d) dsp^2, sp^2, sp^3

39. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1 g?
(a) 2.57×10^{21} unit cells
(b) 5.14×10^{21} unit cells
(c) 1.28×10^{21} unit cells
(d) 1.71×10^{21} unit cells

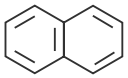
40. Tertiary amine is oxidised to oxide by
(a) $KMnO_4$ (b) H_2O_2
(c) $K_2Cr_2O_7$ (d) all of these.

41. A lanthanoid has n unpaired electrons in f-subshell and has lilac colour. Which colour is likely for another lanthanoid having $14 - n$ unpaired electrons in f-subshell?
(a) White (b) Black
(c) Lilac (d) Complementary of lilac

42. If 340 g of a mixture of N_2 and H_2 in the correct ratio gave 20% yield of NH_3, the mass produced would be
(a) 16 g (b) 17 g
(c) 20 g (d) 68 g

43. The non-aromatic compound among the following is

(a)  (b) 

(c)  (d) 

44. Which of the following gases has least solubility in aq. NaOH solution?

(a) CO_2 (b) SO_2

(c) H_2S (d) NH_3

45. Select the correct order of bond strength.

(a) $O_2 > O_2^+ > O_2^- > O_2^{2-}$

(b) $O_2^{2-} > O_2^- > O_2^+ > O_2$

(c) $O_2^+ > O_2 > O_2^- > O_2^{2-}$

(d) $O_2^{2-} > O_2^- > O_2 > O_2^+$

46. An acid chloride on reaction with H_2/Pd – $BaSO_4$ changes to $(CH_3)_2$ CHCHO. This acid chloride on reaction with CH_3MgBr/H_3O^+ gives

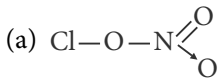
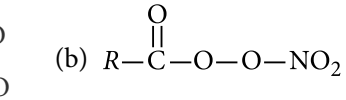
(a) $(CH_3)_3COH$

(b) $(CH_3)_2CHOH$

(c) $(CH_3)_2CHCOCH_3$

(d) $(CH_3)_2CHCHO$

47. Which of the following is not formed at Antarctica?

(a)  (b) 

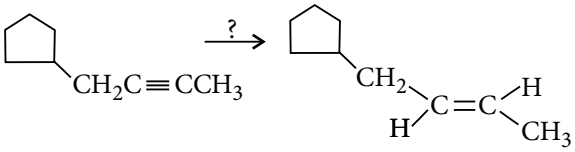
(c) Type-I clouds (d) Polar vortex

48. The mass of 50% (mass/mass) solution of HCl required to react with 100 g of $CaCO_3$ would be

(a) 73 g (b) 100 g

(c) 146 g (d) 200 g

49. Reagent used to convert the following alkyne to alkene is



(a) Pd-C/H_2 (b) Na/NH_3

(c) Ni/H_2 (d) all of these.

50. Which of the following is isostructural with $Cr_2O_7^{2-}$?

(a) $S_2O_7^{2-}$ (b) $S_2O_6^{2-}$

(c) $S_2O_8^{2-}$ (d) $S_2O_5^{2-}$

SOLUTIONS

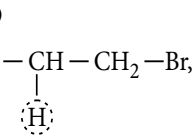
1. **(a)**

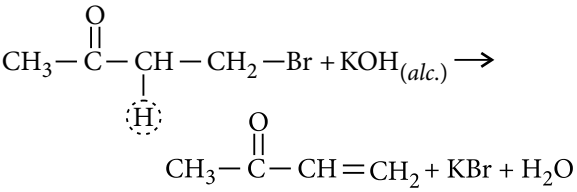
2. **(c) :** $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

3. **(d) :** All the pairs show negative deviations from Raoult's law hence, ΔH_{mixing} and ΔV_{mixing} both are negative.

4. **(b) :** In  the encircled hydrogen is more acidic due to electron withdrawing effect of the  group, therefore it can be easily abstracted by a base. Further, the product formed is stabilized by resonance due to conjugation of the double bond.



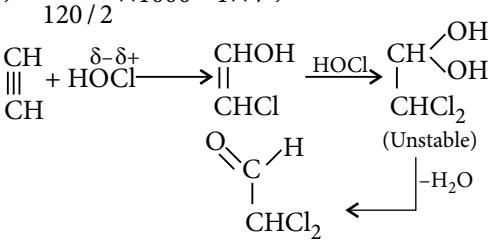
5. **(d) :** The choice (c) is correct for partial hydrolysis and (b) is correct for complete hydrolysis.

$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

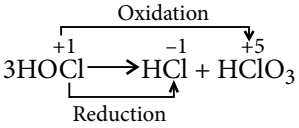
6. **(c) :** meq. of NaH_2PO_4 = meq. of NaOH

Thus, $\frac{12}{120/2} \times 1000 = 1 \times V$; $V =$ 200 mL

7. **(c) :** 

2, 2- Dichloroethanal

8. **(d) :** During disproportionation reaction, same compound undergoes simultaneous oxidation and reduction.

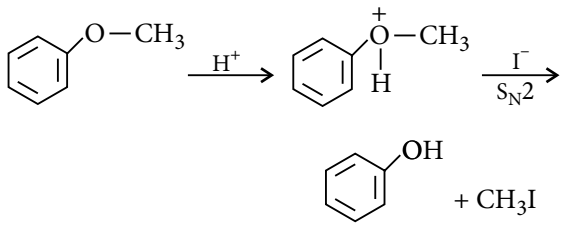


9. **(c) :** No. of atoms of *A* from corners of unit cell = 7/8

No. of atoms of *B* from faces of unit cell = 3

Thus, *A* : *B* = 7/8 : 3 or 7 : 24. Thus, formula is A_7B_{24}.

10. (c) :



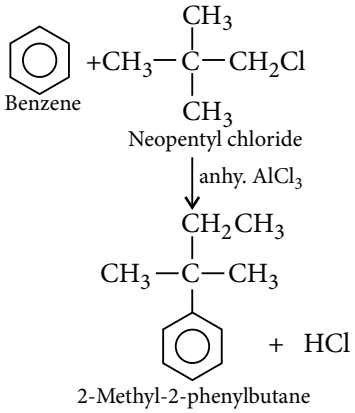
11. (c) : Bead produced with $CaSO_4$ is colourless $Ca(BO_2)_2$, because Ca^{2+} is a colourless ion.

12. (c) : $Z = \dfrac{PV}{nRT}$

$$\frac{PV}{nRT} > 1 \quad \Rightarrow \quad V > \frac{1 \times 0.082 \times 273}{1}$$

$$\Rightarrow \quad V > 22.38 \text{ L}$$

13. (b) :

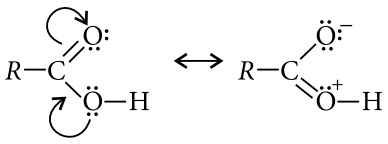


14. (b) : Solubility of hydroxides increases with increase in atomic number down the group.

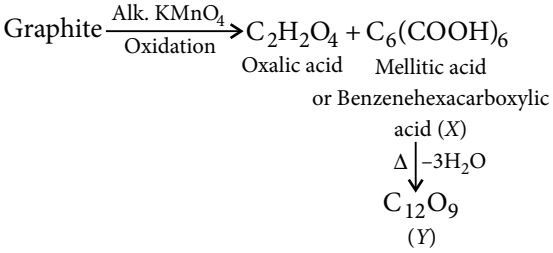
15. (b) : $\Delta G = \Delta H - T\Delta S$

At low T, ΔH and ΔS both are +ve and ΔG is also +ve (non-spontaneous). At high temperature, $T\Delta S > \Delta H$ and ΔG = –ve (spontaneous).

16. (a) :



17. (d) :



18. (d) : Order of reaction = $\frac{1}{3}+\frac{2}{3}=1$.

Unit of rate constant for 1st order reaction = time^{-1}

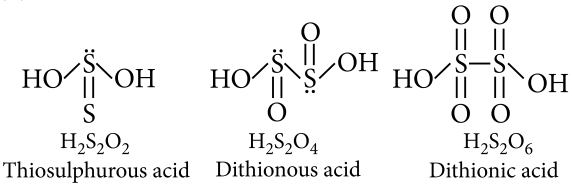
19. (c) : $H-\overset{\overset{O}{\|}}{C}-OH$ reduces Tollens' reagent due to $-\overset{\overset{O}{\|}}{C}-H$ group.

CH_3COOH gives wine red colour of $(CH_3COO)_3Fe$ on reacting with $FeCl_3$.

HCOCl (formed by reaction of HCOOH and $SOCl_2$) is unstable and gives $CO_{(g)}$.

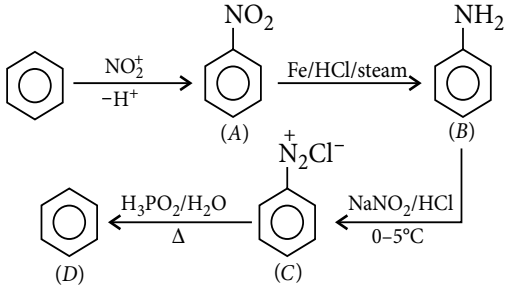
$NaHCO_3$ reacts with both the acids to give the same gas CO_2.

20. (d) :



21. (b) : In a micelle, polar head is at the outer surface and non-polar tail is at the inner surface.

22. (a) :



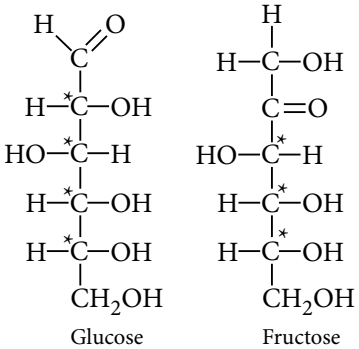
23. (a) : It is Rn which is obtained during nuclear disintegration.

24. (d) : 0.1 M H_2SO_4 will liberate maximum H^+ ions.

25. (b) **26. (b)**

27. (b) : In the titration of strong acid against weak alkali, methyl orange is used as an indicator.

28. (d) :



29. (c) : $Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3\uparrow$
$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2\uparrow$
$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3\uparrow$
$CaO + H_2O \longrightarrow Ca(OH)_2$

30. (c) **31. (a)**

32. (b) : Most stable oxidation state of Ce is = +3 *i.e.*, in $Ce(OH)_3$.

33. (c) : Solubility of AgCl in water, $s_1 = \sqrt{K_{sp}}$
In 0.01 M $CaCl_2$, it is given by

$$K_{sp} = s \times (0.01 \times 2 + s) \quad \therefore \quad s_2 = \frac{K_{sp}}{0.02}$$

In 0.01 M NaCl, it is given by

$$K_{sp} = s \times (0.01 + s) \quad \therefore \quad s_3 = \frac{K_{sp}}{0.01}$$

In 0.05 M $AgNO_3$, it is given by

$$K_{sp} = s \times (0.05 + s) \quad \therefore \quad s_4 = \frac{K_{sp}}{0.05}$$

The solubilities are derived by neglecting s in comparison to 0.02, 0.01 and 0.05.

34. (b) : Orlon is a polymer of vinyl cyanide.

35. (d) : Mond process is used for ref ning of nickel.

36. (a) : $E = \frac{hc}{\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{\lambda}$

$E = 242 \text{ kJ mol}^{-1} = 242 \times 10^3 \text{ J mol}^{-1}$

$= \frac{242\times10^3}{6.02\times10^{23}}$ J per molecule of Cl—Cl bond

$\Rightarrow \quad \frac{6.6\times10^{-34}\times3\times10^{8}}{\lambda} = \frac{242\times10^3}{6.02\times10^{23}}$

$\Rightarrow \quad \lambda = 492.5 \text{ nm}$

37. (a) : Two cysteine molecules covalently link *via* a disulphide bond.

38. (b) : In $[Ni(CO)_4]$, Ni : $3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑ ; $4s^2$ ↑↓ shif s to $3d$ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ acquiring sp^3 -hybridisation.
In $[Ni(CN)_4]^{2-}$, Ni^{2+}: $3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑ shif s to ↑↓ ↑↓ ↑↓ ↑↓ as CN^- is a strong f eld ligand acquires dsp^2-hybridisation.
In $[NiCl_4]^{2-}$, Ni^{2+}: $3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑ acquires sp^3-hybridisation because Cl^- is a weak f eld ligand.

39. (a) : One unit cell in NaCl lattice has 4 NaCl formula units.
4×58.5 g NaCl = 6.02×10^{23} unit cells
(1 mole unit cells)

$$1 \text{ g NaCl} = \frac{6.02\times10^{23}}{4\times58.5} = 2.57 \times 10^{21} \text{ unit cells}$$

40. (b) : $R_3N + [O] \xrightarrow{H_2O_2} R_3N\rightarrow O$
(Amine-*N*-oxide)

41. (c) : For the same number of unpaired electrons, the colour is likely to be very similar.

42. (d) : 20% yield of NH_3 and thus,

$$20\% \text{ of } 340 \text{ g is} = \frac{20\times340}{100} = 68 \text{ g}$$

43. (b)

44. (d) : Basic gas (NH_3) does not dissolve in basic NaOH solution.

45. (c) :

Species	Total e^-s	Bond order
O_2^+	15	2.5
O_2	16	2.0
O_2^-	17	1.5
O_2^{2-}	18	1.0

Bond strength increases on increasing bond order.

46. (c) :

$(CH_3)_2CHCOCl \xrightarrow{Pd-BaSO_4} (CH_3)_2CHCHO + HCl$
An acid chloride → An aldehyde

$+ \; CH_3MgBr$
$\downarrow H_3O^+$

$(CH_3)_2CHCOCH_3$
A ketone

47. (b)

48. (c) : eq. of HCl = eq. of $CaCO_3$

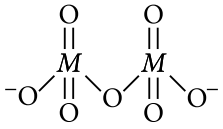
Thus, $\frac{w}{36.5} = \frac{100}{50} \quad \Rightarrow \quad w = 73$ g HCl

50 g HCl is present in 100 g HCl solution and thus, mass of solution required for 73 g HCl

$$= \frac{73\times100}{50} = 146 \text{ g}$$

49. (b) : Birch reduction of non-terminal alkynes with Na/NH_3 gives *trans*-alkenes.

50. (a) : $Cr_2O_7^{2-}$ and $S_2O_7^{2-}$ are isostructural.



Where, M = Cr and S.

CONCEPT BOOSTER

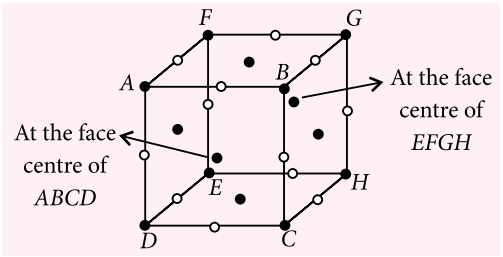
Dear students!! Hope you have started your preparation for competitive examinations. In physical chemistry part of Class XII, maximum students face problems in Solid State. This article will help you in solving problems. Hope you will enjoy it. Take care !!

*Arunava Sarkar

SOLID STATE

1. NH_4Cl crystallizes in a body centred cubic lattice pattern. Edge length of the unit cell is 400 pm and radius of Cl^- is 150 pm. Calculate the radius of the NH_4^+ ion.

2. A solid *XY* has the following crystal structure :



Identify which type of coordination is exhibited here.

3. CsBr has *bcc* type structure where edge length is 5.2 pm. Find out the shortest interionic distance in the structure.

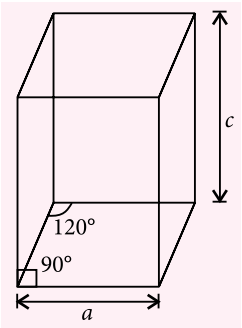
4. A metal '*M*' crystallizes in *bcc* structure. How many 'nearest' and next 'nearest' neighbours does the metal have?

5. An element crystallizes in a *bcc* pattern where the edge length of the unit cell is 0.39 pm. Density of the metal is 0.6 g cm^{-3}. What is the atomic weight of the element?

6. In a crystalline solid, anions '*Z*' are arranged in cubic close packing and forms the structure of the lattice. Cations '*X*' occupy all the tetrahedral holes and cations '*Y*' occupy all the octahedral holes. What will be the formula of the lattice/solid?

7. White tin crystallizes in tetragonal system where $a = b = 510$ pm and $c = 325$ pm. Its density is found to be 4.675 g cm^{-3}. Calculate the number of atoms in the unit cell. (At. wt. of Sn = 119)

8. Given : a = 100 pm, c = 200 pm. A solid metal '*M*' crystallizes in hexagonal close packing pattern as shown in the figure.



Density of the solid metal is 240 g cm^{-3}. How many atoms are there in the given unit cell?

(Given : Avogadro's number = 6.023×10^{23}, Atomic mass of the metal = 250 g mol^{-1})

9. Calculate the radius of the spheres of maximum size that can be exactly fitted in the following voids made by the spheres of radii *R*.

(a) Triangular void (b) Tetrahedral void
(c) Octahedral void (d) Cubic void

10. NaCl has *fcc* lattice. How many ions are in contact with single Na^+ ion?

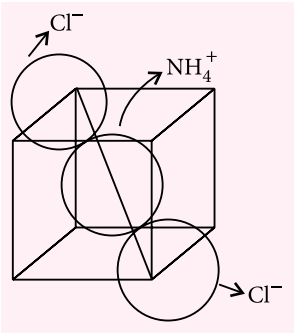
11. The density of diamond is 3.54 g cm^{-3} at 25°C. Calculate the carbon-carbon bond distance in diamond.

12. X-ray diffraction experiment shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What percentage of nickel exists as Ni^{2+}?

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

SOLUTIONS

1.



As it is *bcc*, hence,

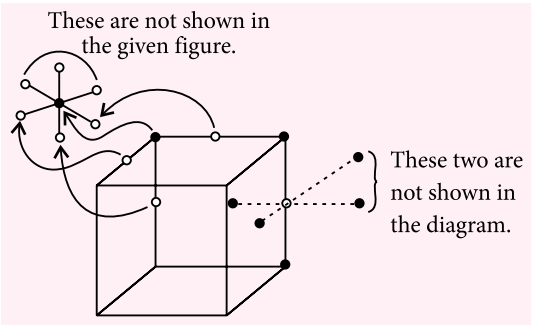
$\sqrt{3}a = 2r_{Cl^-} + 2r_{NH_4^+}$

$\therefore \quad \sqrt{3} \times 400 = (2 \times 150) + 2r_{NH_4^+}$

$\Rightarrow \quad 2r_{NH_4^+} = 392.8\,pm \quad \Rightarrow \quad r_{NH_4^+} = 196.4\,pm$

$\therefore$ Radius of the NH_4^+ ion = 196.4 pm

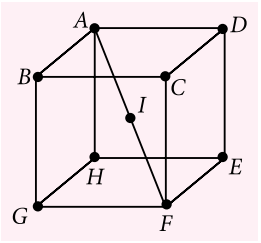
2.



Therefore, it is a 6 : 6 coordination.

3. In *bcc* type structure, shortest interionic distance will be $\frac{a\sqrt{3}}{2} = \frac{5.2 \times \sqrt{3}}{2} = 4.5032$ pm

4.



Take the ball '*A*' as reference. Distance of '*A*' from '*B*' or '*H*' or '*D*' will be equal *i.e.* equal to the edge length *a*.

Now, distance between '*A*' and '*C*' or '*A*' and '*G*' or '*A*' and '*E*' will be equal *i.e.* $a\sqrt{2} = 1.414a$

Distance between '*A*' and '*F*' = $a\sqrt{3} = 1.732a$

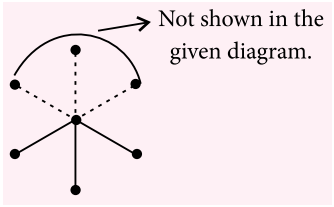
and distance between '*A*' and '*I*' = $\frac{a\sqrt{3}}{2} = 0.866a$

So '*I*' is nearest to '*A*' in the given unit cell. '*A*' is also a part of other 7 unit cells ($\because$ corner atom is shared in between 8 unit cells).

$\therefore$ Nearest neighbours = 8

Next nearest neighbour will be at distance *a*.

i.e.



$\therefore$ Next nearest neighbours = 6

5. $d = \frac{Z \times M}{N_0 \times a^3}$

[Z = no. of atoms in the unit cell, M = molar mass of the element, d = density of the crystal, a = edge length, N_0 = Avogadro's no.]

$\therefore \quad 0.6 = \frac{2 \times M}{6.023 \times 10^{23} \times (0.39 \times 10^{-10})^3}$

[In *bcc*, $Z = 2$]

$\Rightarrow \quad M = \frac{0.6 \times 6.023 \times (0.39)^3 \times 10^{-7}}{2}$

$\Rightarrow \quad M = 0.107 \times 10^{-7}\ g\ mol^{-1}$

6. $Z = 4$ [$\because$ *ccp* ≡ *fcc*]

$\therefore$ Total number of tetrahedral voids = 8

Total number of octahedral voids = 4

$\therefore$ Number of cations, $X = 8$

Number of cations, $Y = 4$

Hence, $X : Y : Z = 8 : 4 : 4 = 2 : 1 : 1$

$\therefore$ Formula of the lattice is X_2YZ.

7. Base area = $a \times b = 510 \times 510 \times 10^{-20}\ cm^2$

$\therefore$ Volume = $(a \times b \times c)$

$= 510 \times 510 \times 10^{-20} \times 325 \times 10^{-10}\ cm^3$

$= 51 \times 51 \times 325 \times 10^{-28}\ cm^3$

$d = \frac{Z \times M}{N_0 \times a^3} = \frac{Z \times M}{N_0 \times (a \times b \times c)}$

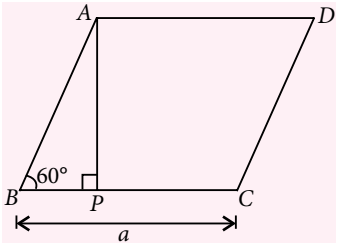
$4.675 = \frac{Z \times 119}{6.023 \times 10^{23} \times 51 \times 51 \times 325 \times 10^{-28}}$

$4.675 = \frac{Z \times 119}{50.91}$

$Z = \frac{4.675 \times 50.91}{119} = 2$

$\therefore$ No. of atoms in the unit cell = 2

8. This is the base part.



$AP \perp BC$ is drawn.

$AB = BC = a$

$\sin 60° = \frac{AP}{AB}$

[In the ΔAPB]

$\Rightarrow \quad AP = AB \sin 60°$

$= a \sin 60°$

Base area $= BC \times AP = a \times a \sin 60°$

$= a^2 \sin 60°$

$\therefore$ Volume $= a^2 \sin 60° \times c$

$$d = \frac{Z \times M}{N_0 \times \text{Volume}}$$

$$240 = \frac{Z \times 250}{6.023 \times 10^{23} \times a^2 \sin 60° \times c}$$

$$240 = \frac{Z \times 250}{6.023 \times 10^{23} \times (100)^2 \times \sin 60° \times 200 \times 10^{-30}}$$

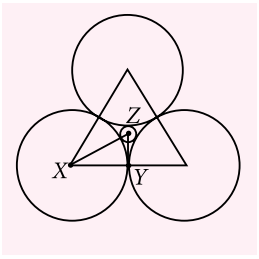
$$240 = \frac{Z \times 250}{6.023 \times 0.866 \times 2 \times 10^{29} \times 10^{-30}}$$

$$240 = \frac{Z \times 250}{10.43 \times 10^{-1}} = Z \times 239.6$$

$$Z = \frac{240}{239.6} \approx 1$$

$\therefore$ No. of atoms in the unit cell = 1

9. (a) Construction of triangular void is as below:



$XZ = R + r$; $XY = R$; $\angle ZXY = 30°$

$$\therefore \quad \cos 30° = \frac{XY}{XZ} = \frac{R}{R+r}$$

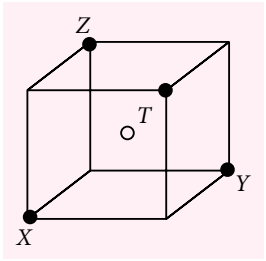
$$\frac{\sqrt{3}}{2} = \frac{R}{R+r} \quad \Rightarrow \quad \frac{R+r}{R} = \frac{2}{\sqrt{3}}$$

$$1 + \frac{r}{R} = \frac{2}{\sqrt{3}} \quad \Rightarrow \quad \frac{r}{R} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

$r = 0.155R$

(b) A tetrahedral void will look like below :

Spheres X and Y are touching each other.



$XY = 2R = \sqrt{2}a$

Sphere taking place the tetrahedral void *i.e.* T is also toucing each other.

Therefore, $XT = R + r = \frac{\sqrt{3}\,a}{2}$

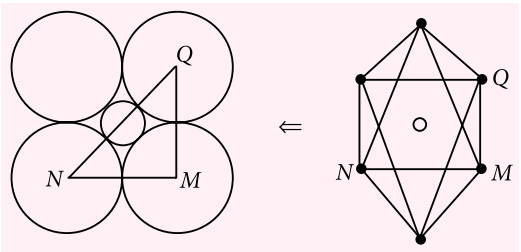
$$\frac{2R}{R+r} = \frac{\sqrt{2}a}{\frac{\sqrt{3}a}{2}} = \frac{2\sqrt{2}a}{\sqrt{3}a} = 2\sqrt{\frac{2}{3}}$$

$$\frac{R+r}{R} = \sqrt{\frac{3}{2}} \quad \Rightarrow \quad \frac{R+r}{R} = 1.2247 \approx 1.225$$

$$1 + \frac{r}{R} = 1.225 \quad \Rightarrow \quad \frac{r}{R} = 0.225$$

$r = 0.225\ R$

(c) An octahedral void will look like below :



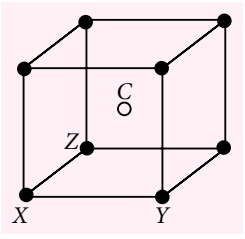
$\angle NQM = 45°$

$$\sin 45° = \frac{MN}{NQ} \quad \Rightarrow \quad \frac{1}{\sqrt{2}} = \frac{2R}{2R+2r} = \frac{R}{R+r}$$

$$\Rightarrow \quad \frac{R+r}{R} = \sqrt{2} \quad \Rightarrow \quad 1 + \frac{r}{R} = 1.414 \quad \Rightarrow \quad \frac{r}{R} = 0.414$$

$\therefore \quad r = 0.414R$

(d) A cubic void will look like below:



Cubic void is at position C.

$$ZC = R + r = \frac{\sqrt{3}\,a}{2}$$

$XY = 2R = a$

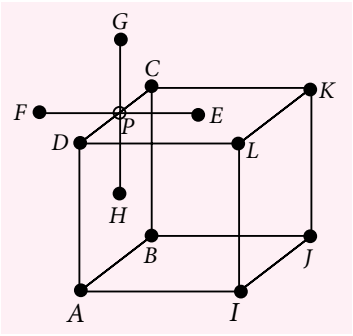
$$\therefore \quad \frac{R+r}{2R}=\frac{\frac{\sqrt{3}\,a}{2}}{a}=\frac{\sqrt{3}\,a}{2a}=\frac{\sqrt{3}}{2}$$

$$2R+2r=2\sqrt{3}R$$

$$2r=2R(\sqrt{3}-1)=2R\times 0.732$$

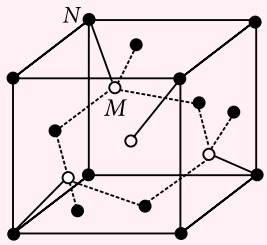
$$r=0.732R$$

10. In *fcc* structure of NaCl, Na^+ ions will be present at the edge centres *i.e.* octahedral voids.
Look at the following diagram :



P is the position of Na^+ ion.
A, *B*, *C*, *D*, *E*, *F*, *G*, *H*, *I*, *J*, *K*, *L* are the positions of Cl^- ions shown in the diagram.
Cl^- ion at '*F*' and '*G*' are belonging to the nearest unit cells, *i.e.* adjacent unit cells (one at the left side and the another at the top of this). But out of these Cl^- ions, only *C*, *D*, *H*, *G*, *E*, *F* are touching the Na^+ ion at *P*. Hence six Cl^- ions are in contact with single Na^+ ion.

11. Diamond has the *fcc* structure and more four atoms are present at the alternate tetrahedral voids.



● → Diamond atoms (either at the face centres or at the corners)
○ → Diamond atoms at the alternate tetrahedral voids

So, total diamond atoms

$$=\left(8\times\frac{1}{8}\right)+\left(6\times\frac{1}{2}\right)+4=8$$

$$\therefore \quad Z=8$$

$$d=\frac{Z\times M}{N_0\times a^3} \Rightarrow 3.54=\frac{8\times 12}{6.023\times 10^{23}\times a^3}$$

$$a^3=\frac{96}{3.54\times 6.023\times 10^{23}}$$

$$a^3=4.5025\times 10^{-23} \Rightarrow a=3.5575\times 10^{-8}$$

$$\therefore \quad a=3.5575 \text{ Å}$$

To check carbon-carbon distance, the shortest one which is a tetrahedral void carbon and its nearest corner is taken as in the diagram *M* and *N*.

$$MN=\frac{a\sqrt{3}}{4}=\frac{3.5575\times 1.732}{4} \text{ Å} = 1.5403 \text{ Å}$$

12. As the formula is $Ni_{0.98}O_{1.00}$, hence it suggests metal deficiency defect. As per the formula, for every 100 oxide ions there are 98 nickel ions. Nickel ions can be in the form of either Ni^{2+} or Ni^{3+}. Suppose, out of 98 nickel ions, *x* are Ni^{2+}. Hence (98 – *x*) are Ni^{3+}.
Therefore,

$$\underbrace{x\times 2+(98-x)3}_{\text{Total positive charge}}=\underbrace{100\times 2}_{\text{Total negative charge}} \quad \left\{\begin{array}{l}\text{Compound is}\\ \text{electrically}\\ \text{neutral}\end{array}\right\}$$

$$\Rightarrow \quad 2x+294-3x=200 \Rightarrow x=94$$

$$\therefore \quad 94 \text{ are } Ni^{2+}.$$

$$\therefore \quad \%\text{ of } Ni^{2+}=\frac{94}{98}\times 100=95.9183\%$$

CHEMISTRY MUSING

SOLUTION SET 22

1. (a): $Fe_2(C_2O_4)_3 \rightleftharpoons \underset{1\text{ mol}}{2Fe^{3+}} + \underset{3\text{ mol}}{3C_2O_4^{2-}}$

Only $C_2O_4^{2-}$ is oxidised by MnO_4^-,

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

5 mol of $C_2O_4^{2-} \equiv 2$ mol of MnO_4^-

$\therefore$ 3 mol of $C_2O_4^{2-} \equiv \frac{2}{5}\times 3 = \frac{6}{5}$ mol of MnO_4^-

$FeC_2O_4 \rightleftharpoons Fe^{2+} + C_2O_4^{2-}$

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

---

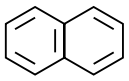
5 mol of $FeC_2O_4 \equiv 3$ mol of MnO_4^-

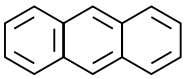
1 mol of $FeC_2O_4 \equiv \frac{3}{5}$ mol of MnO_4^-

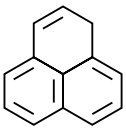
1 mol of $Fe_2(C_2O_4)_3 \equiv \frac{6}{5}$ mol of MnO_4^-

Thus, ratio of MnO_4^- required by 1 mol of $Fe_2(C_2O_4)_3$ and $FeC_2O_4 = 2 : 1$.

2. (c): (1)  ; 12 σ, 3 π $\Rightarrow \frac{12}{3} = 4$

(2)  ; 19 σ, 5 π $\Rightarrow \frac{19}{5} = 3.8$

(3)  ; 26 σ, 7 π $\Rightarrow \frac{26}{7} = 3.71$

(4)  ; 25 σ, 6 π $\Rightarrow \frac{25}{6} = 4.166$

The increasing order of σ/π bond ratio is

(3) < (2) < (1) < (4).

3. (c): $Fe^{2+} + e^- \longrightarrow Fe^+$

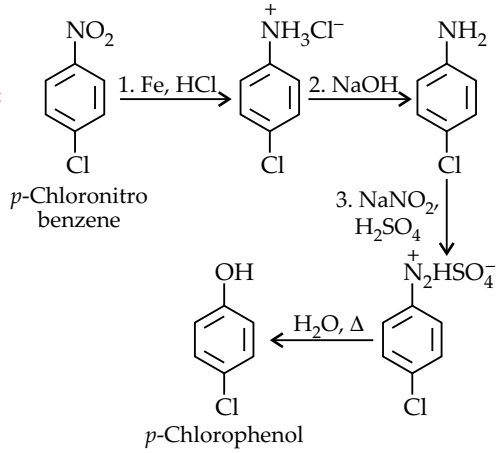
$NO \longrightarrow NO^+ + e^-$

Based on magnetic properties of the complex, it is found that iron has three unpaired electrons thus, it is present as Fe^+ formed by reduction of Fe^{2+} by NO which is oxidised to NO^+.

4. (b): $2Na^+_{(aq)} + 2I^-_{(aq)} + HgI_{2(s)} \longrightarrow 2Na^+_{(aq)} + HgI^{2-}_{4(aq)}$

The number of mole particles decreases from $4(2Na^+ + 2I^-)$ to $3(2Na^+ + HgI_4^{2-})$. Hence, the colligative property will decrease or, the vapour pressure of solution will increase to a constant value until NaI is completely consumed.

5. (b):



6. (a)

7. (b): Heat transferred to the calorimeter

= Heat capacity of the calorimeter × Rise in temperature

= 17.7 kJ K^{-1} × (0.5 K) = 8.85 kJ

Molar mass of $CH_4 = 12 + 4 = 16$ g mol^{-1}

Enthalpy of combustion of CH_4 at constant volume

$(i.e., \Delta E) = -\left(\frac{8.85}{0.16}\times 16\right) = -885$ kJ mol^{-1}

8. (a): $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

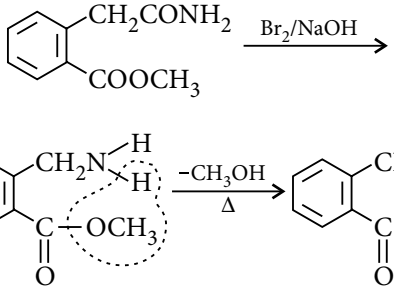
$\Delta H = \Delta E + \Delta n_g RT$

$= -885 + (-2 \times 8.314 \times 10^{-3} \times 300)$

$= -885 - 4.988$

$= -889.988$ kJ mol^{-1}

9. (1):



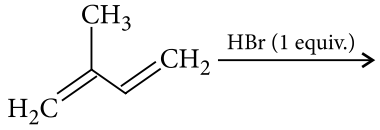
10. (8)

WBJEE SOLVED PAPER 2015

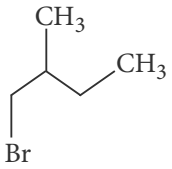
Arunava Sarkar, West Bengal

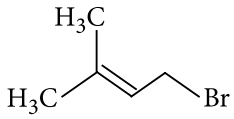
Category I (Q.1 to Q.30)

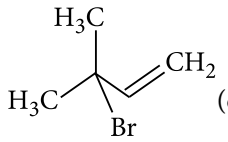
Each question has one correct option and carries 1 mark, for each wrong answer 1/4 mark will be deducted.

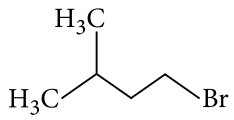
1. 

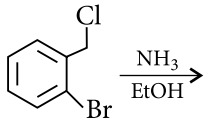
The major product of the above reaction is

(a) 

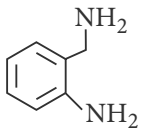
(b) 

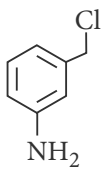
(c) 

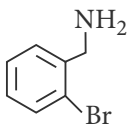
(d) 

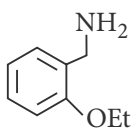
2. 

The product of the above reaction is

(a) 

(b) 

(c) 

(d) 

3. For the reaction $A + 2B \longrightarrow C$, the reaction rate is doubled if the concentration of A is doubled. The rate is increased by four times when concentrations of both A and B are increased by four times. The order of the reaction is

(a) 3 (b) 0
(c) 1 (d) 2

4. At a certain temperature, the value of the slope of the plot of osmotic pressure (π) against concentration (C in mol L^{-1}) of a certain polymer solution is $291R$. The temperature at which osmotic pressure is measured is (R is gas contant)

(a) 271°C (b) 18°C
(c) 564 K (d) 18 K

5. The *rms* velocity of CO gas molecules at 27°C is approximately 1000 m/s. For N_2 molecules at 600 K the *rms* velocity is approximately

(a) 2000 m/s (b) 1414 m/s
(c) 1000 m/s (d) 1500 m/s

6. A gas can be liquefied at temperature T and pressure P provided

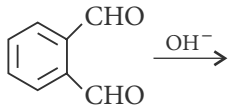
(a) $T = T_c$ and $P < P_c$ (b) $T < T_c$ and $P > P_c$
(c) $T > T_c$ and $P > P_c$ (d) $T > T_c$ and $P < P_c$

7. In a mixture, two enantiomers are found to be present in 85% and 15% respectively. The enantiomeric excess (e, e) is

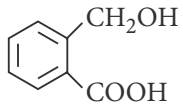
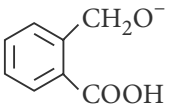
(a) 85% (b) 15%
(c) 70% (d) 60%

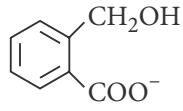
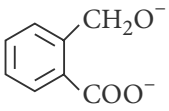
8. 1,4-Dimethylbenzene on heating with anhydrous $AlCl_3$ and HCl produces

(a) 1,2-dimethylbenzene
(b) 1,3-dimethylbenzene
(c) 1,2,3-trimethylbenzene
(d) ethylbenzene.

9. 

The product of the above reaction is

(a)  (b) 

(c)  (d) 

10. Suppose the mass of a single Ag atom is '*m*'. Ag metal crystallizes in *fcc* lattice with unit cell of length '*a*'. The density of Ag metal in terms of '*a*' and '*m*' is

(a) $\frac{4m}{a^3}$ (b) $\frac{2m}{a^3}$

(c) $\frac{m}{a^3}$ (d) $\frac{m}{4a^3}$

11. For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 300 K, the value of $\Delta G°$ is –690.9 *R*. The equilibrium constant value for the reaction at that temperature is (*R* is gas constant)

(a) 10 atm^{-1} (b) 10 atm

(c) 10 (d) 1

12. At a particular temperature the ratio of equivalent conductance to specific conductance of a 0.01 (N) NaCl solution is

(a) 10^5 cm^3 (b) 10^3 cm^3

(c) 10 cm^3 (d) 10^5 cm^2

13. The units of surface tension and viscosity of liquids are respectively

(a) kg $m^{-1}s^{-1}$, N m^{-1} (b) kg s^{-2}, kg $m^{-1}s^{-1}$

(c) N m^{-1}, kg $m^{-1}s^{-2}$ (d) kg s^{-1}, kg $m^{-2}s^{-1}$

14. The ratio of volumes of CH_3COOH 0.1 (N) to CH_3COONa 0.1 (N) required to prepare a buffer solution of pH 5.74 is (given : pK_a of CH_3COOH is 4.74)

(a) 10 : 1 (b) 5 : 1

(c) 1 : 5 (d) 1 : 10

15. The reaction of methyltrichloroacetate (Cl_3CCO_2Me) with sodium methoxide (NaOMe) generates

(a) carbocation (b) carbene

(c) carbanion (d) carbon radical.

16. Best reagent for nuclear iodination of aromatic compounds is

(a) KI/CH_3COCH_3 (b) I_2/CH_3CN

(c) KI/CH_3COOH (d) I_2/HNO_3

17. In the Lassaigne's test for the detection of nitrogen in an organic compound, the appearance of blue coloured compound is due to

(a) ferric ferricyanide

(b) ferrous ferricyanide

(c) ferric ferrocyanide

(d) ferrous ferrocyanide.

18. In the following reaction :

$RMgBr + HC(OEt)_3 \xrightarrow{\text{Ether}} \xrightarrow{H_3O^+} P$

The product '*P*' is

(a) *R*CHO (b) R_2CHOEt

(c) R_3CH (d) $RCH(OEt)_2$

19. The dispersed phase and dispersion medium of fog respectively are

(a) solid, liquid (b) liquid, liquid

(c) liquid, gas (d) gas, liquid.

20. The decreasing order of basic character of K_2O, BaO, CaO and MgO is

(a) $K_2O > BaO > CaO > MgO$

(b) $K_2O > CaO > BaO > MgO$

(c) $MgO > BaO > CaO > K_2O$

(d) $MgO > CaO > BaO > K_2O$

21. In aqueous alkaline solution, two electron reduction of HO_2^- gives

(a) HO^- (b) H_2O

(c) O_2 (d) O_2^-

22. Cold ferrous sulphate solution on absorption of NO develops brown colour due to the formation of

(a) paramagnetic $[Fe(H_2O)_5(NO)]SO_4$

(b) diamagnetic $[Fe(H_2O)_5(N_3)]SO_4$

(c) paramagnetic $[Fe(H_2O)_5(NO_3)](SO_4)_2$

(d) diamagnetic $[Fe(H_2O)_4(SO_4)]NO_3$

23. Amongst Be, B, Mg and Al the second ionization potential is maximum for

(a) B (b) Be

(c) Mg (d) Al

24. Sulphuryl chloride (SO_2Cl_2) reacts with white phosphorus (P_4) to give

(a) PCl_5, SO_2 (b) $OPCl_3$, $SOCl_2$

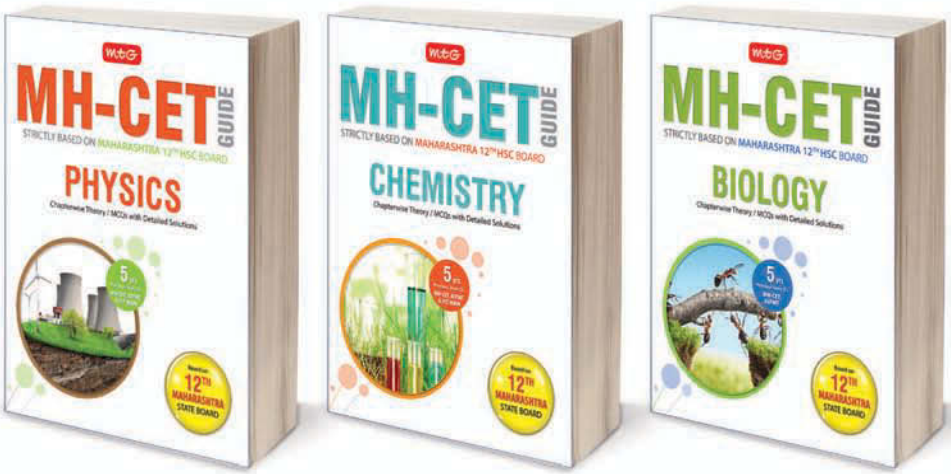
(c) PCl_5, SO_2, S_2Cl_2 (d) $OPCl_3$, SO_2, S_2Cl_2

Presenting

The best self scorer Guides for

MH-CET

STRICTLY BASED ON **MAHARASHTRA 12TH HSC** BOARD



₹350/- ₹300/- ₹350/-

The wait is over!!! The most reliable and updated source for MH-CET entrance exam is now available. An excellent blend of accuracy with authenticity, these books focus on all the basic needs of a student to efficiently prepare for the exam. With comprehensive theory, exhaustive practice and actual MCQs, these books are the best self scorer guides for every PMT aspirant. So no more waiting, go grab your copy today and ensure your seat in MH-CET.

HIGHLIGHTS

- Strictly based on Maharashtra 12th HSC Board textbooks
- Synopsis of chapters complemented with concept maps
- Simple and lucid language with additional information
- MCQs divided in two levels: Level - I and Level - II (Some tough questions of higher standard to make the students aware of them.)
- 6000+ chapterwise MCQs with detailed explanations
- Previous years' (2014 - 2010) MCQs of MH-CET, AIPMT and JEE Main*

*In Physics and Chemistry only

Visit **www.mtg.in** for latest offers and to buy online!

mtG Learning Media

Available at all leading book shops throughout the country.
For more information or for help in placing your order:
Call 0124-4951200 or email:info@mtg.in

25. The number of lone pairs of electrons on the central atoms of H_2O, $SnCl_2$, PCl_3 and XeF_2 respectively, are
(a) 2, 1, 1, 3 (b) 2, 2, 1, 3
(c) 3, 1, 1, 2 (d) 2, 1, 2, 3

26. Consider the following salts: NaCl, $HgCl_2$, Hg_2Cl_2, $CuCl_2$, CuCl and AgCl. Identify the correct set of insoluble salts in water.
(a) Hg_2Cl_2, CuCl, AgCl
(b) $HgCl_2$, CuCl, AgCl
(c) Hg_2Cl_2, $CuCl_2$, AgCl
(d) Hg_2Cl_2, CuCl, NaCl

27. In the following compound, the number of '*sp*' hybridized carbon is

$$CH_2{=}C{=}CH{-}\underset{\displaystyle CN}{\underset{|}{CH}}{-}C{\equiv}CH$$

(a) 2 (b) 3
(c) 4 (d) 5

28. Match the flame colours of the alkaline earth metal salts in the Bunsen burner.

(p) Calcium	1. Brick red
(q) Strontium	2. Apple green
(r) Barium	3. Crimson

(a) p-1, q-3, r-2 (b) p-3, q-1, r-2
(c) p-2, q-3, r-1 (d) p-1, q-2, r-3

29. Extraction of gold (Au) involves the formation of complex ions '*X*' and '*Y*'.

$$\text{Gold ore} \xrightarrow[CN^-,\, H_2O,\, O_2]{\text{Roasting}} HO^- + X \xrightarrow{Zn} Y + Au$$

'*X*' and '*Y*' are respectively
(a) $Au(CN)_2^-$ and $Zn(CN)_4^{2-}$
(b) $Au(CN)_4^{3-}$ and $Zn(CN)_4^{2-}$
(c) $Au(CN)_3^-$ and $Zn(CN)_6^{4-}$
(d) $Au(CN)_4^-$ and $Zn(CN)_3^-$

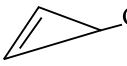
30. The atomic number of cerium (Ce) is 58. The correct electronic configuration of Ce^{3+} ion is
(a) $[Xe]4f^1$ (b) $[Kr]4f^1$
(c) $[Xe]4f^{13}$ (d) $[Kr]4d^1$

Category II (Q.31 to Q.35)

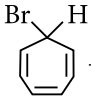
Each question has one correct option and carries 2 marks, for each wrong answer 1/2 mark will be deducted.

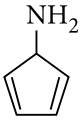
31. Roasted copper pyrite on smelting with sand produces
(a) $FeSiO_3$ as fusible slag and Cu_2S as matte
(b) $CaSiO_3$ as infusible slag and Cu_2O as matte
(c) $Ca_3(PO_4)_2$ as fusible slag and Cu_2S as matte
(d) $Fe_3(PO_4)_2$ as infusible slag and Cu_2S as matte.

32. The total number of aromatic species generated in the following reactions is

(i)  $+ SbCl_5 \longrightarrow$

(ii)  + Sodium metal $\xrightarrow{THF}$

(iii)  $+ H_2O \longrightarrow$

(iv)  $\xrightarrow{HNO_2}$

(a) zero (b) 2
(c) 3 (d) 4

33. For the reaction $X_2Y_{4(l)} \longrightarrow 2XY_{2(g)}$ at 300 K the values of ΔU and ΔS are 2 kcal and 20 cal K^{-1} respectively. The value of ΔG for the reaction is
(a) –3400 cal (b) 3400 cal
(c) –2800 cal (d) 2000 cal

34. At temperature of 298 K the emf of the following electrochemical cell :

$$Ag_{(s)}|Ag^+(0.1\ M)||Zn^{2+}(0.1\ M)|Zn_{(s)}$$

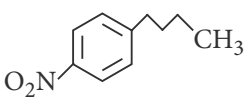
will be (given $E^\circ_{cell} = -1.562$ V)
(a) –1.532 V (b) –1.503 V
(c) 1.532 V (d) –3.06 V

35. Addition of sodium thiosulphate solution to a solution of silver nitrate gives '*X*' as white precipitate, insoluble in water but soluble in excess thiosulphate solution to give '*Y*'. On boiling in water, '*Y*' gives '*Z*'. '*X*', '*Y*' and '*Z*' respectively, are
(a) $Ag_2S_2O_3$, $Na_3[Ag(S_2O_3)_2]$, Ag_2S
(b) Ag_2SO_4, $Na[Ag(S_2O_3)_2]$, Ag_2S_2
(c) $Ag_2S_2O_3$, $Na_5[Ag(S_2O_3)_3]$, AgS
(d) Ag_2SO_3, $Na_3[Ag(S_2O_3)_2]$, Ag_2O

Category III (Q.36 to Q.40)

Each question has one or more correct option(s), choosing which will fetch maximum 2 marks on pro rata basis. However, choice of any wrong option(s) will fetch zero mark for the question.

36. Identify the correct method for the synthesis of the compound shown below from the following alternatives.

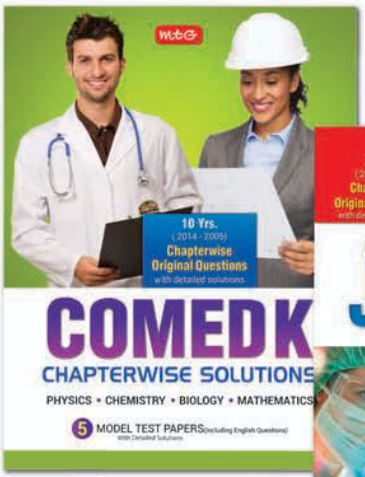


IMPORTANT **ANNOUNCEMENT** for **PMT/PET aspirants**

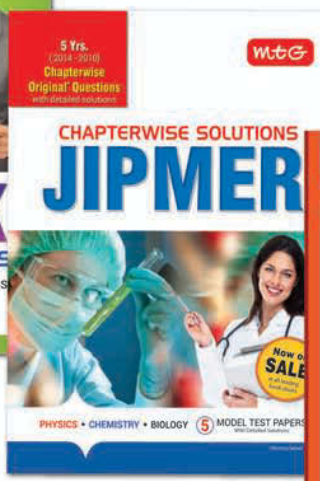
Your Search for

Authentic Past Papers | Error-Free Solutions | Veri-Similar Practice Papers

IS OVER !!

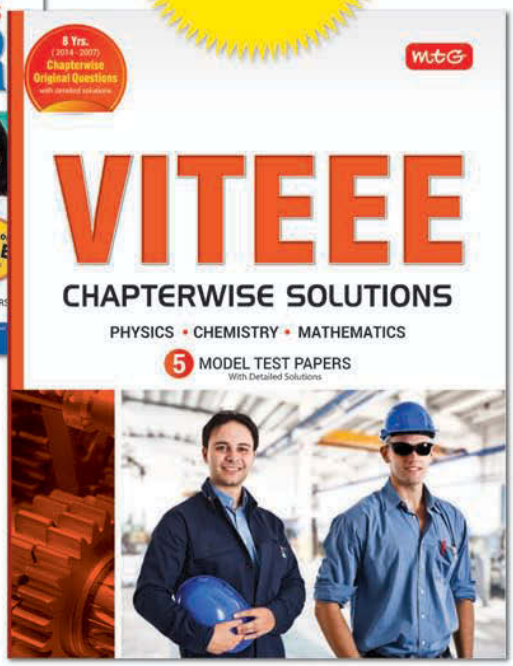


Rs. 375/-

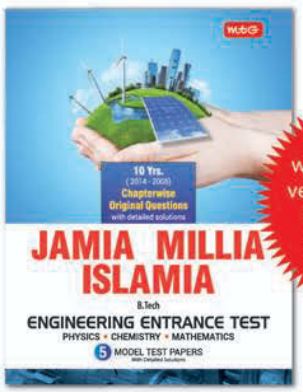


Rs. 300/-

Now on **SALE**



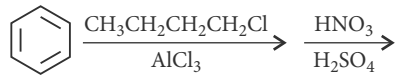
Rs. 275/-

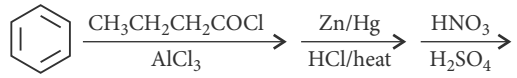


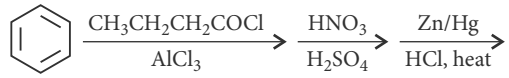
IN PRESS will be **ON SALE** very soon in your town/city at your nearest bookshop.

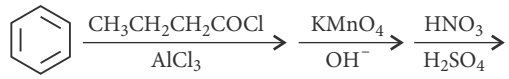
mtG

IT's WORTH WAITING FOR AUTHENTIC PAST PAPERS | ERROR-FREE SOLUTIONS

(a) 

(b) 

(c) 

(d) 

37. Within the list shown below, the correct pair of structures of alanine in pH ranges 2-4 and 9-11 is

I. $H_3N^+—CH(CH_3)CO_2H$

II. $H_2N—CH(CH_3)CO_2^-$

III. $H_3N^+—CH(CH_3)CO_2^-$

IV. $H_2N—CH(CH_3)CO_2H$

(a) I, II (b) I, III

(c) II, III (d) III, IV

38. The increase in rate constant of a chemical reaction with increasing temperature is(are) due to the fact(s) that

(a) the number of collisions among the reactant molecules increases with increasing temperature

(b) the activation energy of the reaction decreases with increasing temperature

(c) the concentration of the reactant molecules increases with increasing temperature

(d) the number of reactant molecules acquiring the activation energy increases with increasing temperature.

39. Optical isomerism is exhibited by (*ox* = oxalate anion, *en* = ethylenediamine)

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$

(b) $[Co(en)_3]^{3+}$

(c) *trans*-$[CrCl_2(ox)_2]^{3-}$

(d) $[Co(ox)(en)_2]^+$

40. Ionization potential values of noble gases decrease down the group with increase in atomic size. Xenon forms binary fluorides by the direct reaction of elements. Identify the correct statement(s) from below.

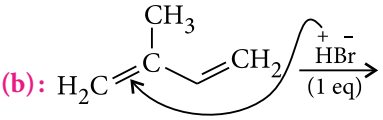
(a) Only the heavier noble gases form such compounds.

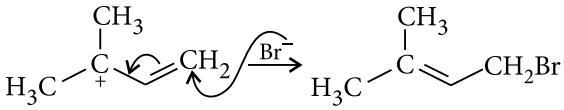
(b) It happens because the noble gases have higher ionization energies.

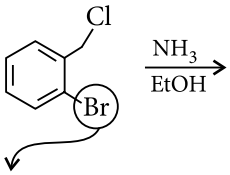
(c) It happens because the compounds are formed with electronegative ligands.

(d) Octet of electrons provide the stable arrangements.

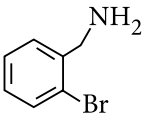
SOLUTIONS

1. (b): 



2. (c): 

[This $-\ddot{B}\ddot{r}:$ takes part in resonance and generates a partial double bond character with benzene ring. Hence, only –Cl will be substituted.]

$\therefore$ Product is 

3. (c): $A + 2B \rightarrow C$

Reaction rate is doubled when the concentration of *A* is doubled. Again when both *A* and *B* are made four times, reaction rate also becomes four times. It means reaction rate is independent of the concentration of *B*. With respect to *A*, the order is definitely one.

$\therefore$ w.r.t. *A*, order = 1

w.r.t. *B*, order = 0

Overall order = 1

4. (b): $\pi = CRT$

$\Rightarrow \dfrac{\pi}{C} = RT$

But, slope $\dfrac{\pi}{C} = 291\,R$

$\therefore \quad RT = 291R \Rightarrow T = 291\text{ K}$

$\therefore \quad T = (291 - 273)°C = 18°C$

5. (b): $C = \sqrt{\dfrac{3RT}{M}}$

$$\frac{C_{CO}}{C_{N_2}} = \sqrt{\frac{3RT_{CO}}{M_{CO}} \times \frac{M_{N_2}}{3RT_{N_2}}}$$

$$\Rightarrow \frac{1000}{C_{N_2}} = \sqrt{\frac{300}{28} \times \frac{28}{600}} \Rightarrow C_{N_2} = 1000 \times \sqrt{2}$$

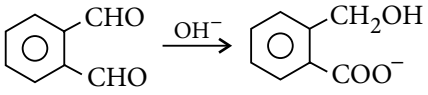
$\Rightarrow C_{N_2} = 1000 \times 1.414 = 1414$ m/s

6. (b): The two very important conditions for liquifying a gas are

1. Temperature should be lower than the critical temperature ($T < T_c$).
2. Pressure should be greater than the critical pressure ($P > P_c$).

7. (c) : Enantiomeric excess is (85 – 15) = 70%.

8. (a) : This is an isomerisation reaction which takes place in the presence of $AlCl_3$ and HCl. From *para*-dimethylbenzene, *ortho*-dimethylbenzene is produced.

9. (c) : 

It is an intramolecular Cannizzaro reaction.

10. (a) : $$\text{Density} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$
$$= \frac{\text{No. of atoms} \times \text{Mass of each atom}}{\text{Volume of the unit cell}}$$
$$= \frac{4 \times m}{a^3} \quad (\because \text{ in } fcc, \text{ no. of atoms} = 4)$$

11. (a) : $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$\Delta G = -RT \ln K$

$-690.9\ R = -RT \ln K$

$\frac{690.9}{300} = \ln K$

$2.303 = \ln K$

$2.303 = 2.303 \log K$

$K = 10^1$

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \cdot p_{O_2}} \times \frac{atm^2}{atm^3} = atm^{-1}$$

12. (a) : $\lambda = \kappa \times \frac{1000}{N}$

$$\Rightarrow \quad \frac{\lambda}{\kappa} = \frac{ohm^{-1}cm^2\ g\ eq^{-1}}{ohm^{-1}cm^{-1}} = cm^3\ g\ eq^{-1}$$

$$\Rightarrow \quad \frac{\lambda}{\kappa} = \frac{1000}{N} = \frac{1000}{10^{-2}\ g\ eq} = 10^5\ cm^3 g\ eq^{-1}$$

13. (b) : $$\text{Surface tension} = \frac{\text{Force}}{\text{Length}} = \frac{N}{m}$$
$$= \frac{kg\ m\ s^{-2}}{m} = kg\ s^{-2}$$

$$F = \eta A \cdot \frac{dv}{dx}$$

$$\Rightarrow \quad \eta = \frac{F}{A \cdot \frac{dv}{dx}}$$

$$\Rightarrow \quad \eta = \frac{N}{m^2 \times \frac{m\ s^{-1}}{m}} = N\ m^{-2}\ s$$
$$= kg\ m\ s^{-2}\ m^{-2}\ s = kg\ m^{-1}s^{-1}$$

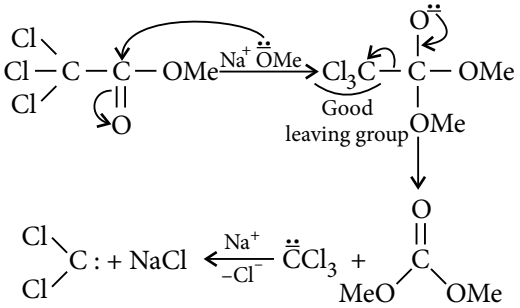
14. (d) : $$pH = pK_a + \log_{10} \frac{\text{Activity of salt}}{\text{Activity of acid}}$$

$$\Rightarrow \quad 5.74 = 4.74 + \log_{10} \frac{\text{Concentration} \times \text{Volume}_{(salt)}}{\text{Concentration} \times \text{Volume}_{(acid)}}$$

[Concentrations given are same]

$$\Rightarrow \quad 1 = \log_{10} \frac{V_{salt}}{V_{acid}} \quad \Rightarrow \quad V_{salt} : V_{acid} = 10 : 1$$

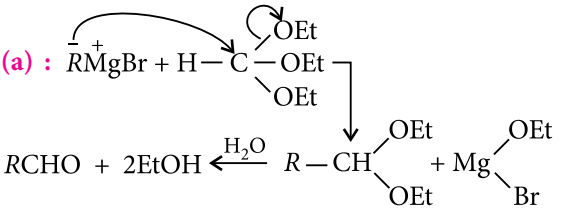
$$\therefore \quad V_{acid} : V_{salt} = 1 : 10$$

15. (b) : 

Therefore, the product is carbene.

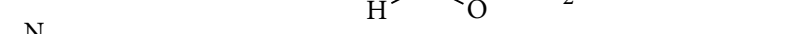
16. (d) : Iodination should be done in the presence of a strong oxidising agent.

17. (c) : Ferric ferrocyanide is the correct answer.

18. (a) : 

19. (c) : For fog, dispersed phase is liquid and dispersion medium is gas.

20. (a) : Alkali metal oxides are very much basic. Down the group in the alkaline earth metal series, ionisation potential decreases.

21. (a) : 

22. (a) : Brown ring is $[Fe(H_2O)_5(NO)]SO_4$.

23. (a) : $B(5) \rightarrow 1s^2\ 2s^2\ 2p^1$

In second ionization potential electron has to be removed from 2*s*.

It is quite high energetic.

24. (a) : $P_{4(s)} + 10SO_2Cl_{2(l)} \longrightarrow 4PCl_{5(s)} + 10SO_{2(g)}$

25. (a) : $H_2\ddot{O}$ (O is group 16), $\ddot{S}nCl_2$ (Sn is group 14), $\ddot{P}Cl_3$ (P is group 15); $:\ddot{X}eF_2$ (Xe is group 18).

26. (a)

27. (c) : $CH_2=\underset{\downarrow sp}{C}=CH-\underset{\underset{\downarrow sp}{C\equiv N}}{CH}-\underset{\searrow sp}{C}\equiv CH$

28. (a)

29. (a) : $4Au_{(s)} + 8CN^-_{(aq.)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 4[Au(CN)_2]^-_{(aq.)} + 4OH^-_{(aq.)}$

$2[Au(CN)_2]^-_{(aq.)} + Zn_{(s)} \longrightarrow 2Au_{(s)} + [Zn(CN)_4]^{2-}_{(aq.)}$

30. (a) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^0 5s^2 5p^6$

Stable xenon core ($Z = 54$)

For $Z = 56$, it will be $[Xe]6s^2$

In lanthanum ($Z = 57$), electrons should enter in $4f$ but to maintain stable xenon core it will go into $5d$ (difference is little in between $4f$ and $5d$).

But in cerium (Ce, $Z = 58$), electron enters into $4f$.

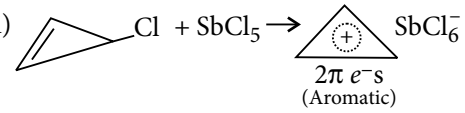
$\therefore \quad Ce^{3+} = [Xe]4f^1$

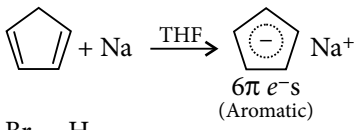
31. (a) : The roasted copper pyrite contains Cu_2S and FeO and some unreacted FeS. Roasted ore on smelting with sand (silica, SiO_2) forms fusible ferrous silicate slag, $FeSiO_3$.

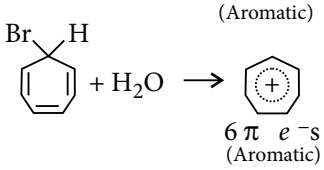
$FeO + SiO_2 \longrightarrow FeSiO_3$

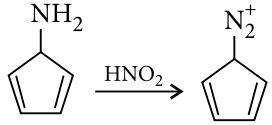
Silica — Ferrous silicate (Slag)

The lower molten layer consists of Cu_2S as copper matte.

32. (c) : (i) 

(ii) 

(iii) 

(iv) 

33. (c) : $\Delta H = \Delta U + \Delta n_g RT$

$\Rightarrow \quad \Delta H = 2000 + 2 \times 2 \times 300$

$[\because \Delta n_g = 2 - 0 = 2, R = 2 \text{ cal } K^{-1} \text{ mol}^{-1}]$

$= 3200$ cal

$\Delta G = \Delta H - T\Delta S = 3200 - (300 \times 20) = -2800$ cal

34. (a) : $2Ag_{(s)} \longrightarrow 2Ag^+ (0.1\text{ M}) + 2e^-$

$2e^- + Zn^{2+} (0.1\text{ M}) \longrightarrow Zn_{(s)}$

$2Ag_{(s)} + Zn^{2+} (0.1\text{ M}) \longrightarrow 2Ag^+ (0.1\text{ M}) + Zn_{(s)}$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \cdot \log_{10} \frac{[Ag^+]^2}{[Zn^{2+}]}$$

$$\therefore \quad E_{cell} = -1.562 - \frac{0.0591}{2} \log_{10} \frac{(0.1)^2}{0.1}$$

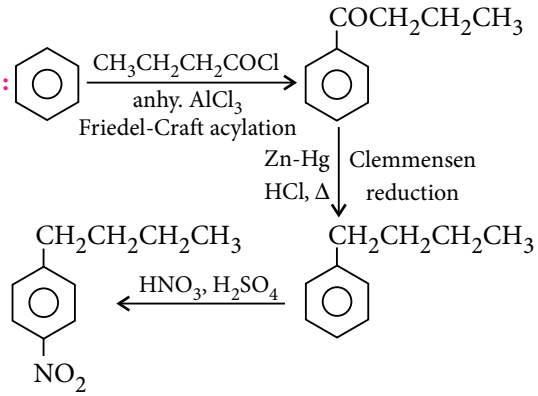
$= -1.562 - 0.03 \log_{10} 10^{-1}$

$\Rightarrow \quad E_{cell} = -1.562 + 0.03 = -1.532$ V

35. (a) : $2AgNO_3 + Na_2S_2O_3 \xrightarrow{(-2NaNO_3)} \underset{(X)\text{ (white ppt.)}}{Ag_2S_2O_3}$

$Ag_2S \xleftarrow{H_2O,\ \Delta} \underset{(Y)\text{ soluble}}{Na_3[Ag(S_2O_3)_2]} \xleftarrow{\text{excess } Na_2S_2O_3}$

Ag_2S (Z)

36. (b) : 

37. (a) : $H_2N-\underset{\underset{CH_3}{|}}{CH}-COOH$

Acidic medium : $H_3\overset{+}{N}-\underset{\underset{CH_3}{|}}{CH}-\underset{\text{Unaffected in acidic medium}}{(COOH)}$

Basic medium : $\underset{\text{Unaffected in basic medium}}{(H_2N)}-\underset{\underset{CH_3}{|}}{CH}-COO^-$

38. (a, d)

39. (a, b, d) : (c) has plane of symmetry.

40. (a, c) : Having high ionization energy, inert gases do not form compounds. Inert gas compounds are hypervalent in nature. So no question of octet fill up through compound formation.

YOU ASK WE ANSWER

Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. Can the stains of mustard oil be removed using potassium permanganate or any other oxidising agent?

Akshay Kumar (Bhagalpur, Bihar)

Ans. Mustard contains turmeric which gives it a beautiful colour, and also acts like a dye. Because of this, it can be very difficult to remove the stain. Some chemicals, like alcohol, hydrogen peroxide, vinegar and perchloroethylene can be used for removing stains at home. There are several oxidative discharge agents used in the textile industry like sodium hypochlorite, sodium chlorite and potassium permanganate, etc. which are not recommended at all for use at home.

Potassium permanganate is a strong oxidising agent when dissolved in water.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

The manganese oxide (MnO_2) left behind by potassium permanganate reactions is deep brown in colour and this reagent is used industrially to discharge indigo-dyed denims, but it is extremely poisonous and also becomes dangerously explosive if its solution is left to dry up.

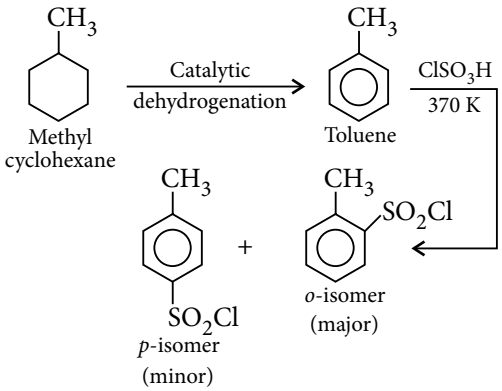
Apart from these, ammonia (NH_3) is also not used for removing the stains from clothes. It reacts with turmeric (the ingredient in mustard) that makes it yellow and hence, making the stain permanent.

Q2. Saccharin (550 times sweeter than sugar) is a well known sweetening agent and a sugar substitute in foods and beverages. On the other hand, chloramine-T is an antiseptic and a mild disinfectant used in hospitals, laboratories where control of pathogens is required. How can these two compounds be obtained from a single organic compound?

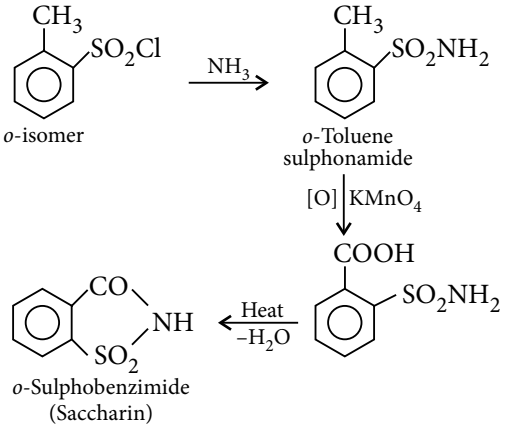
Shipra Chopra (Punjab)

Ans. Saccharin and chloramine-T, both of these compounds can be prepared from methyl cyclohexane as follows :

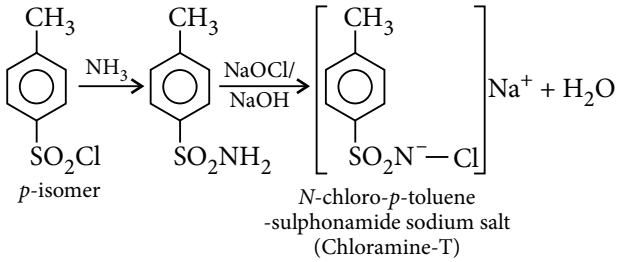
Catalytic dehydrogenation of methyl cyclohexane gives toluene which on treatment with chlorosulphonic acid yields a mixture of *ortho* and *para*-toluenesulphonyl chloride.



Ortho-isomer reacts with ammonia and potassium permanganate to give saccharin.



Para-isomer reacts with ammonia and NaOCl/NaOH to give chloramine-T.



Boost your fundamentals with MTG's Objective series

KEY FEATURES:

All problems 1100+ are new and veri-similar to what you will face in JEE.

Point-wise theory and formulae for last minute revision.

Extremely useful for JEE (Main & Advanced), State Level PETs & PUC also.

Deep knowledge and crystal clear understanding of fundamentals is key to success. MTG's Objective series is created keeping just this insight in mind for Class XI & XII students preparing to compete in entrance exams. Put together by MTG's renowned editorial team, these unique books ensure students get just the start they need.

HIGHLIGHTS:

- 5,255+ pages covering the latest syllabus of AIPMT and other entrance exams
- Check-Your-Grasp questions for self-assessment
- NCERT xtract from NCERT books
- Question Banks including questions from previous years' test papers (solved) of various exams like AIIMS, AIPMT, NEET, AFMC, BHU, AMU, J&K CET, UGET-Manipal, Odisha, UP-CPMT, WB JEE, Kerala PMT, etc.
- Detailed solutions to MCQs for clear understanding
- Additional information for students for exams such as AIIMS, AIPMT, AMU, etc.

*Scan now with your smartphone or tablet**

Visit **www.mtg.in** for latest offers and to buy online!

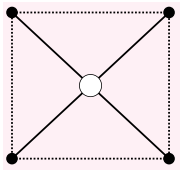
mtG Learning Media

Available at all leading book shops throughout the country.
For more information or for help in placing your order:
Call 0124-4951200 or email info@mtg.in

**Application to read QR codes required*

OLYMPIAD PROBLEMS

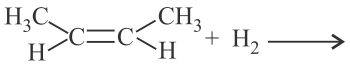
1. With four bonded pairs as given in ball-stick model that represents the shape or structure of different species with different hybridizations, total number of possible hybridisations can be

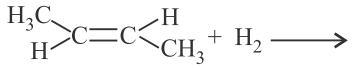


(a) two (b) four
(c) six (d) eight.

2. Minimum amount of heat is evolved in

(a) $CH_3CH_2CH{=}CH_2 + H_2 \longrightarrow$

(b)  $+ H_2 \longrightarrow$

(c)  $+ H_2 \longrightarrow$

(d) $CH_2{=}CH{-}CH{=}CH_2 + 2H_2 \longrightarrow$

3. Consider the following statements :

I. Isotonic solutions have the same molar concentration at a given temperature.

II. The molal elevation constant, K_b is characteristic of a solvent, and is independent of the solute added.

III. The freezing point of a 0.1 M aqueous KCl solution is more than that of a 0.1 M aqueous $AlCl_3$ solution.

Which of these statements is correct?

(a) I and II (b) II and III
(c) I and III (d) I, II and III

4. Among the following, the correct set of ketones capable of giving yellow precipitate with both 2, 4-dinitrophenylhydrazine as well as with alkaline solution of I_2 is

(i) butanone
(ii) propanone
(iii) 3-pentanone
(iv) 2,2-dimethyl-3-pentanone

(a) (i), (ii) and (iii) (b) (ii) and (iv)
(c) (i) and (ii) (d) (i), (ii) and (iv)

5. If equal volumes of 1 M $KMnO_4$ and 1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe(II) to Fe(III) in acidic medium, then Fe(II) oxidised will be

(a) more by $KMnO_4$
(b) more by $K_2Cr_2O_7$
(c) equal in both cases
(d) cannot be determined.

6. In which of the following triplets all the three members are diamagnetic?

(a) B_2, CO, NO^+ (b) Cu^+, O_2^{2-}, O_2
(c) N_2^{2-}, O_2^{2+}, NO^- (d) O_3, N_2^{2+}, N_2O

7. Which of the following conditions would favour the rearrangement of carbocation?

(a) Aqueous medium
(b) Aqueous medium containing dissolved Cl^- ions
(c) Concentrated H_2SO_4
(d) Alcoholic medium

8. If we take 10 litres of a gas at STP, which of the following new conditions will keep the volume constant?

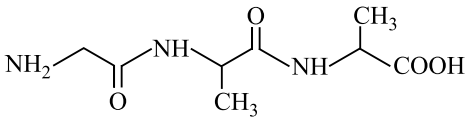
(a) 273 K and 2 atm pressure
(b) 273°C and 2 atm pressure
(c) 546°C and 0.5 atm pressure
(d) 0°C and 0.0 atm pressure

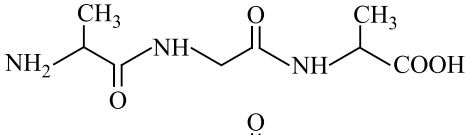
9. $MCrO_{4(s)} \xrightarrow{CH_3COOH_{(aq.)}} MCrO_{4(\text{suspension})}$

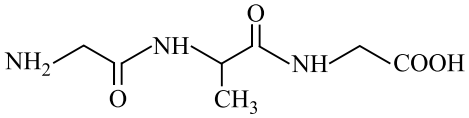
The above change is correct for which of the metal ion(s)?

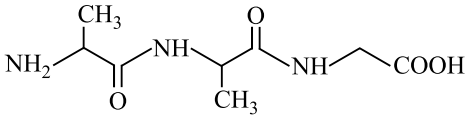
(a) Ba^{2+}, Sr^{2+}, Ca^{2+} (b) Ba^{2+}, Sr^{2+}
(c) Only Ba^{2+} (d) Sr^{2+}, Ca^{2+}

10. A tripeptide is written as Glycine–Alanine–Glycine. The correct structure of the tripeptide is

(a) 

(b) 

(c) 

(d) 

11. Which compound does not contain sp^3 hybridised boron?

(a) Product of the reaction of H_3BO_3 and aqueous solution of sodium hydroxide

(b) Borax

(c) 1 : 1 adduct of BF_3 and NH_3

(d) None of the above

12. In the reactions,

$$CO + 1/2\ O_2 \longrightarrow CO_2$$
$$N_2 + O_2 \longrightarrow 2NO$$

10 mL of a mixture containing carbon monoxide and nitrogen required 7 mL of oxygen to form CO_2 and NO, on combustion. The volume of N_2 in the mixture will be

(a) $\frac{7}{2}$ mL (b) $\frac{17}{2}$ mL

(c) 4 mL (d) 7 mL

13. Glycerol is obtained from propylene ($CH_3 - CH = CH_2$) by using the following reagents.

I. Cl_2 II. Na_2CO_3

III. HOCl IV. NaOH

Correct sequence in which these reagents are used is

(a) II, I, IV, III (b) II, I, III, IV

(c) I, II, IV, III (d) I, II, III, IV

14. In basic medium, H_2O_2 acts as an oxidising agent in its reactions with

(a) $K_3[Fe(CN)_6]$ (b) Ag_2O

(c) $Cr_2(SO_4)_3$ (d) $K_2Cr_2O_7$

15. Which one of the following sets of units represents the smallest and largest amount of energy respectively?

(a) J and erg (b) erg and cal

(c) cal and eV (d) eV and lit-atm

16. The enolic form of butanone contains

(a) 12 σ bonds, 1 π bond and 2 lone pairs of electrons

(b) 11 σ bonds, 1 π bond and 2 lone pairs of electrons

(c) 12 σ bonds, 1 π bond and 1 lone pair of electrons

(d) 10 σ bonds, 2 π bonds and 2 lone pairs of electrons.

17. If order of the size of lanthanoid ions is $P^{3+} > Q^{3+} > R^{3+} > S^{3+}$ then *P*, *Q*, *R* and *S* are respectively

(a) Ce, Pm, Eu, Lu (b) Lu, Eu, Pm, Ce

(c) Pm, Ce, Lu, Eu (d) Lu, Ce, Pm, Eu

18. To obtain an isotope of a given radioactive element, the element must emit

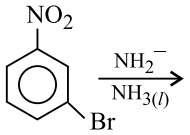
(a) one alpha and one beta particles

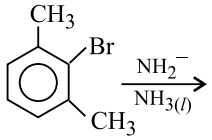
(b) one alpha and two beta particles

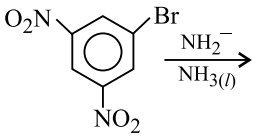
(c) two alpha and two beta particles

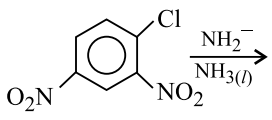
(d) two alpha and four beta particles.

19. In which of the following cases the benzyne mechanism would not operate?

(a) 

(b) 

(c) 

(d) 

20. Which of the following statements is correct regarding XeF_6?

(a) It acts as Lewis acid when it reacts with RbF.

(b) It undergoes complete hydrolysis to give XeO_3.

(c) It fluorinates silica (SiO_2) to give $XeOF_4$.

(d) All of the above.

21. Of the elements Sr, Zr, Mo, Cd and Sb, all of which belong to 5th period the ones that are paramagnetic are

(a) Sr, Cd and Sb (b) Zr, Mo and Cd
(c) Sr, Zr and Cd (d) Zr, Mo and Sb

22. Which of the following is used in the treatment of blood cancer?

(a) I^{131} (b) P^{32}
(c) Rn^{222} (d) I^{127}

23. Ions present in KIBrCl are

(a) K^+, $[IBrCl]^-$ (b) K^{3+}, I^-, Br^-, Cl^-
(c) $[KIBr]^+$, Cl^- (d) K^+, Br^- and ICl

24. An example of an auto-catalytic reaction is

(a) the decomposition of nitroglycerine
(b) thermal reaction between $KClO_4$ and MnO_2
(c) break down of ^{14}C
(d) hydrogenation of vegetable oil using nickel catalyst.

25. Polymer used in bullet proof glass is

(a) PMMA (b) Lexan
(c) Nomex (d) Kevlar.

26. Choose the correct statement.

(a) $[Co(NH_3)_6]^{2+}$ is oxidised to diamagnetic $[Co(NH_3)_6]^{3+}$ by the oxygen in air.
(b) Tetrahedral complexes are more stable than octahedral complexes.
(c) $[Fe(CN)_6]^{3-}$ is less stable but $[FeF_6]^{3-}$ is more stable.
(d) The $[Cu(NH_3)_4]^{2+}$ ion has a tetrahedral geometry and is diamagnetic.

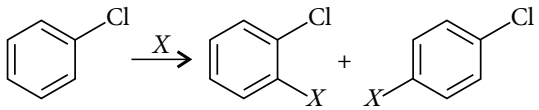
27. Nitrogen tetraoxide (N_2O_4) decomposes as :

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$$

If the pressure of N_2O_4 falls from 0.50 atm to 0.32 atm in 30 minutes, the rate of appearance of $NO_{2(g)}$ is

(a) 0.006 atm min^{-1} (b) 0.003 atm min^{-1}
(c) 0.012 atm min^{-1} (d) 0.024 atm min^{-1}

28.



The para to ortho product ratio is highest when *X* is

(a) NO_2^+ (b) Cl^+
(c) Br^+ (d) SO_3

29. A deliquescent white crystalline hydroxide '*X*' reacts with a nitrate '*Y*' to form another hydroxide which decomposes to give an insoluble brown layer of its oxide. '*X*' is a powerful cautery and breaks down the proteins of skin flesh to a pasty mass. *X* and *Y* are respectively

(a) NaOH, $AgNO_3$ (b) NaOH, $Zn(NO_3)_2$
(c) NaOH, $Al(NO_3)_3$ (d) $Ca(OH)_2$, $Hg(NO_3)_2$

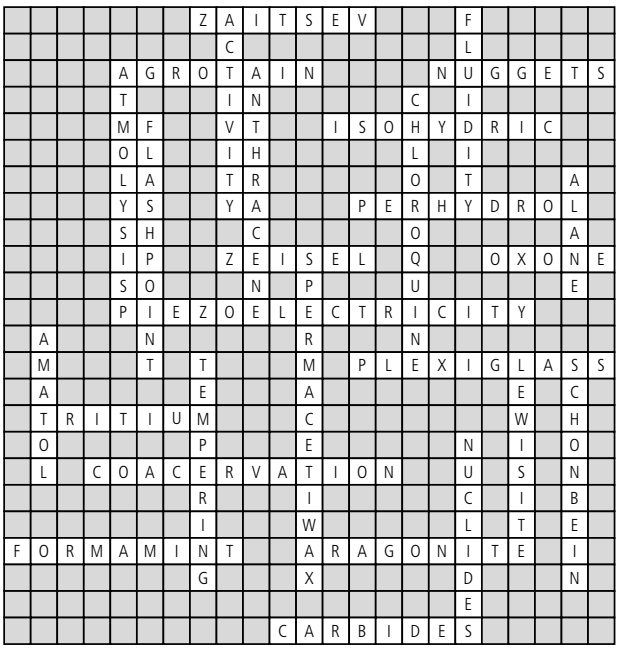
30. Glucose molecule reacts with *x* number of molecules of phenylhydrazine to yield osazone. The value of *x* is

(a) three (b) two
(c) one (d) four.

ANSWER KEYS

1.	(a)	**2.**	(d)	**3.**	(d)	**4.**	(c)	**5.**	(b)
6.	(d)	**7.**	(c)	**8.**	(b)	**9.**	(c)	**10.**	(c)
11.	(d)	**12.**	(c)	**13.**	(d)	**14.**	(c)	**15.**	(d)
16.	(a)	**17.**	(a)	**18.**	(b)	**19.**	(b)	**20.**	(d)
21.	(d)	**22.**	(b)	**23.**	(a)	**24.**	(a)	**25.**	(b)
26.	(a)	**27.**	(c)	**28.**	(d)	**29.**	(a)	**30.**	(a)

SOLUTIONS TO MAY 2015 CROSSWORD



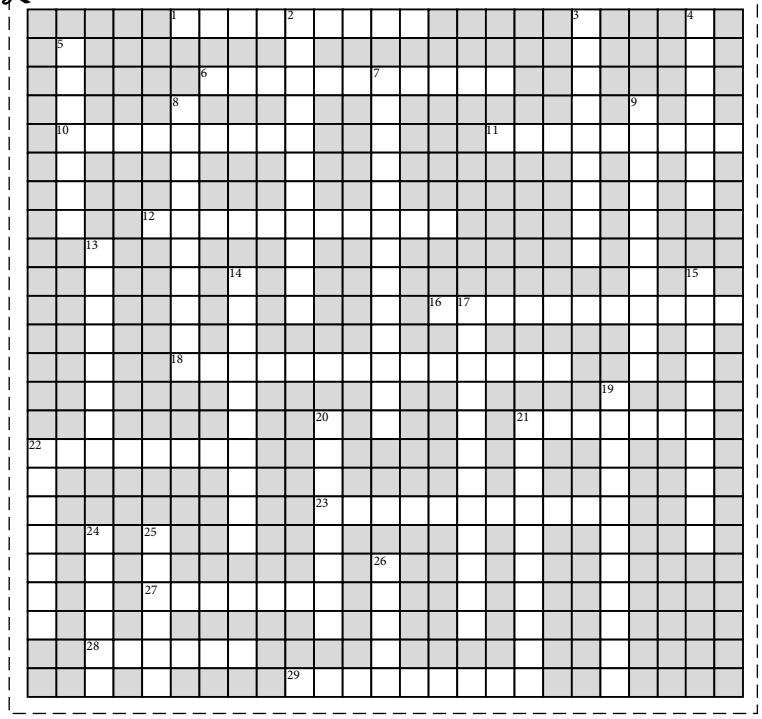
Winners of May 2015 Crossword

- **Apurva Joshi (Gujarat)**
- **Vandana Pandey (New Delhi)**
- **Priyadarshani K. (Kerala)**

CROSS WORD

Readers can send their answer with complete address before 15th of every month to win exciting prizes.
Winners' name with their valuable feedback will be published in next issue.

Cut Here



ACROSS

1. Diamide of carbonic acid. (9)

6. Colloidal solutions in which the dispersed phase has very little affinity for the dispersion medium. (11)

10. Kinetic theory of gases was given by _____. (9)

11. Minerals having single silicate chains. (9)

12. Another name of non-stoichiometric solid. (11)

16. An alcohol-water mixture containing 57.1% of ethyl alcohol by volume. (11)

18. Chemical name of water glass. (14)

21. Polymer formed from ethylene chloride and sodium polysulphide. (7)

22. The region of maximum electron density in an orbital. (8)

23. Heterocyclic polyethers with atleast four oxygen atoms. (11)

27. Optically active enzyme present in almonds. (7)

28. The shape of azide ion. (6)

29. A region of continuous absorption or emission of radiations without any line structure. (9)

DOWN

2. Solvents which have the tendencies to accept as well as donate protons. (11)

3. Coordination complexes of NO with transition metals. (9)

4. A cork like substance produced by heating acetylene in the presence of spongy copper. (7)

5. Hardest known artificial substance. (7)

7. A counter that detects nuclear radiations from flashes of light generated in a material by the radiations. (13)

8. Substances added to help in attachment of the ore particles to air bubbles in froth floatation process. (10)

9. Joining together of two ice cubes on pressing. (10)

13. The air temperature at which the relative humidity reaches 100%. (8)

14. Electron deficient species in which nitrogen has a sextet of electrons. (10)

15. Another name of cyclic ketals or acetals. (10)

17. Alkaline solution of sodium potassium tartrate. (12)

19. Spin quantum number was given by____. (11)

20. The metallic sound produced due to irregular burning of the fuel. (8)

21. First man-made element. (10)

22. A hard powder obtained by heating Al_2O_3 in an electric arc. (7)

24. Furnace used for annealing of gold. (6)

25. Spontaneous destabilisation of colloidal solution. (6)

26. Cylindrical bar of impure metal used in zone refining method. (5)